

# Green Chemistry and Engineering Conference Proceedings

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**Proceedings**

**1997 Green Chemistry  
and Engineering Conference**

**Implementing Vision 2020  
for the Environment**

June 23-25, 1997

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and Engineering Conference**

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Implementing Vision 2020 for the Environment

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1997 Green Chemistry &  
Engineering Conference

**Implementing Vision 2020 for the Environment**

June 23-25, 1997

# **PLENARY SESSION**



**DR. JOSEPH ALEXANDER'S SPEECH  
AT THE  
1997 GREEN CHEMISTRY AND ENGINEERING CONFERENCE**

There are a number of reasons, as I hope you know, that EPA has an interest in the area of green chemistry and engineering. Our Office of Pollution Prevention and Toxic Substances manages the Green Chemistry Challenge, a Presidential re-invention initiative. And as you know, the awards for the Green Chemistry Challenge will be given in an event here tomorrow evening.

Second, the Office of Research and Development, as part of its strategy for dealing with environmental risk management, sponsors a research program in the area of green chemistry and engineering under our extramural research grants activity called STAR, Science To Achieve Results.

For the past three years now, we have partnered with the National Science Foundation in running a competition for grants awards in this area. In the first two years of that program, you might be interested, we funded 44 awards for a total of nearly 12 million dollars. In an extremely competitive program, those 44 winners were selected from over 400 proposals that we and NSF received in the first two years. Awards for the third year of the program will be announced shortly, having just gone through peer review this spring and early summer.

The Green Chemistry and Engineering Conference is a meeting that is very important to us and one that, as you've heard, we hope will become a continuing series, an opportunity for top scientists in government, industry, and academia to talk together about these kinds of issues and to identify research needs and priorities that, for example, are a response to the industry's Technology Vision 2020. So I hope that this is the beginning of a new forum for a true collaboration.

I might end by quoting from Jack Gibbons, the Assistant to the President for Science and Technology who has said, "Together we must transform our technological infrastructure to use less energy and less materials to cause less environmental harm and at the same time, to provide those goods and services that we all desire. In this joint endeavor, we seek more than small steps down the familiar technological paths. Instead we need a transformation of our industrial economy." Certainly the topics that you all will be discussing today and tomorrow and Wednesday morning are relevant there.

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**DR. E. WILLIAM COLGLAZIER'S SPEECH  
AT THE  
1997 GREEN CHEMISTRY AND ENGINEERING CONFERENCE**

Good morning. Let me also welcome you here to the National Academy of Sciences, National Academy of Engineering, Institute of Medicine and the National Research Council. We're very pleased that the Conference on Green Chemistry and Engineering and the presentation of awards from the competition are being held here in our facility.

This is an area that's of great interest to the Academy complex as well as to me personally. Before I came to work at the Academy in 1991, I was at the University of Tennessee. One of the research centers at the university in the mid-'80s that I helped create was a partnership of chemical engineers, environmental engineers and environmental lawyers. It was the Center on Clean Products and Clean Technologies which still exists today and is doing good work.

Also, in the mid-'80s, we helped the state of Tennessee to create a program to grant awards in pollution prevention, copying the pollution prevention programs that were begun in other states. So I think this is a very important initiative personally, the emphasis on using science and technology for environmental benefit.

The topic is also of great interest to the Academy complex. Most of our work is doing studies on various topics, primarily for the U.S. Government, but also for other sponsors. The Academy complex does have an endowment, although it's small - in terms of the funds that it generates - compared to our overall external funding per year.

But those funds are quite precious to us. The presidents of the three academies use them for the topics that we think are the most important to support. Sometimes these funds are used for studies the government is reluctant to initiate. They are also used to explore certain thematic initiatives that we feel are important for society, for the country and for the globe.

It is in this area dealing with the environmental issues and sustainable development that the presidents of the three academies have put a fair amount of their endowment income over the last few years, doing such things as helping to support a new board on sustainable development. This new board contains distinguished individuals from science, engineering and other fields, including past government service. They are looking at not only what needs to be done in the U.S., but also around the globe to help make the transition to sustainable development in the next century.

The work of this board is also assisted by our disciplinary and special topic boards that emphasize issues which fit quite well with the theme of this conference. The Board on Chemical Sciences and Technology is one such board. It's our board that has most of our chemistry expertise in the Academy complex. We also have the Board on Environmental Sciences and Toxicology as well as the National Academy of Engineering itself carrying out projects related to green chemistry and green engineering.

So it's a distinct pleasure to have this meeting here at the Academy complex. I look forward personally to the presentations over the next day. And we look forward, I hope, to having you back in another year. Thank you.

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**DR. PAUL S. ANDERSON'S SPEECH  
AT THE  
1997 GREEN CHEMISTRY AND ENGINEERING CONFERENCE**

On behalf of the American Chemical Society, I want to join my colleagues in welcoming you to this exciting national research conference on green chemistry and engineering. You are among the growing number of people who understand that chemists and engineers can have a significant impact on improving the environment by "reinventing" how chemicals and materials are produced and used.

This is an exciting endeavor that looks beyond controlling waste at the end of a process, and instead challenges us to look at the entire life-cycle of chemical production and create new ways to more efficiently produce useful products with less waste or preferably no waste. The importance of devoting adequate resources and attention to this critical object needs to be promoted within our companies, universities, and laboratories. We must do this. We must convince people that sustainable living is an achievable goal. We must develop the science and technology that will allow us to consume at a rate that is in balance with what the earth can produce and dispose of waste in a manner that is in balance with what the earth can process and assimilate. This conference promises to give us some ammunition to help convince our colleagues and the public that green chemistry and engineering works — both in terms of environmental improvement and economic viability. Green chemistry truly means "innovations for a cleaner world."

This year's conference in part focuses on the recent report, *Technology Vision 2020: The US. Chemical Industry*. The development of this report began with a request from the White House Office of Science and Technology Policy for industry input regarding how the U.S. government could better allocate R&D funding to advance the manufacturing base of the U.S. economy. What resulted was this broad study by over 200 technical and business leaders in the

U.S. chemical industry about the factors affecting the competitiveness of the industry in a rapidly changing business environment. The report called, *Vision 2020*, focuses on the technology that is needed to maintain the industry's strong competitive advantage while protecting and improving the environment.

The *Vision 2020* report is important because it is a first of its kind for the chemical industry. It was produced for and by the chemical industry, with input from government and academe. The report was developed by the American Chemical Society, the American Institute of Chemical Engineers, the Chemical Manufacturers

Association, the Council for Chemical Research, and the Synthetic Organic Chemical Manufacturers Association — all of whom are sponsors of this conference.

The report also emphasizes the importance of partnership, and this conference is an excellent step in that direction. Throughout the next three days we will hear about contributions being made by industry, academe, professional societies, and the government to help industry incorporate more green chemistry into practice.

*Technology Vision 2020* presents an outline for strengthening the U.S. chemical industry and preserving its global competitive advantages well into the next century. Many of the vision statements included in the report have an environmental theme. I'd like to take a minute to read these eight vision statements, and I encourage you to visualize the role that environmental issues play in each statement.

- The U.S. Chemical Industry leads the world in technology development, manufacturing, and profitability.
- The U.S. Chemical Industry is responsible for breakthroughs in R&D that enhance the quality of life worldwide by improving energy use, transportation, food, health, housing, and environmental stewardship.
- The U.S. Chemical Industry sets the world standard for excellence of manufacturing operations that allow it to meet the evolving needs of its customers.
- The U.S. Chemical Industry is welcomed by communities worldwide because the industry is a responsible neighbor who protects environmental quality, improves economic well-being, and promotes a higher quality of life.
- The U.S. Chemical Industry sets the standard in the manufacturing sector for efficient use of energy and raw materials.
- The U.S. Chemical Industry works in seamless partnerships with academe and government creating "virtual" laboratories for originating and developing innovative technologies.
- The U.S. Chemical Industry promotes sustainable development by investing in technology that protects the environment and stimulates industrial growth while balancing economic needs with financial constraints.

These, of course, are vision statements. Commitment, action plans, and R&D will be required to achieve this vision. One exciting example is the Chemical Manufacturers Association program called *Responsible Care*® which has already achieved many of its goals for reduced production and release of waste.

The chemical industry is often not fully recognized for the valuable contributions that it makes to U.S. society. Environmental problems of the past are what get much of the attention. A world without the chemical industry, however, would lack modern medicine, transportation, communications, and consumer products. The chemical industry is more diverse than virtually any other U.S. industry. Chemicals are a keystone of U.S. manufacturing, essential to most other industries such as pharmaceuticals, automobiles, textile, furniture, paint, paper, electronics, agriculture, construction, appliances, and services. More than 9,000 corporations develop, manufacture, and market chemical products and processes. Chemicals, therefore, are building blocks for products that meet our most fundamental needs for food, shelter, and health, as well as products vital to the high technology world of computing, telecommunications, and biotechnology.

The economic impact of the chemical industry is significant. In addition to supporting other U.S. industries, the U.S. chemical industry runs one of the largest trade surpluses of any industrial sector and employs more than one-million people. Overall, this industry is the third largest manufacturing sector in the nation, representing approximately 10 percent of all U.S. manufacturing.

The outstanding success of the chemical industry is largely due to scientific and technological breakthroughs and innovations brought about through R&D. In fact, the Institute for the Future notes that the chemical industry is one of the eight most research-intensive industries. This conference hopes to challenge the R&D community in the area of the environment where there are enormous opportunities for improved technology and productivity. This is an appropriate challenge because environmental stewardship is so evident in the Vision 2020 document. As we all know, unsaleable by-products (waste) are common in the chemical production. A less visible but equally important problem is the large amount of energy that is consumed in manufacturing chemicals. New technology is needed for more energy efficient production of chemicals and useful products derived from them. New chemistry is needed for efficient conversion of sustainable biomass into creative new products and for more

efficient generation of existing products from petroleum feed stocks. Each of these objectives represents an intellectual challenge and an opportunity for innovation.

All sectors of the chemical enterprise have something to contribute and benefit from by jointly focusing on green chemistry and engineering. The government wins by supporting a strong U.S. industry that has a positive impact on the economy and jobs, and also helps improve the environment. Academia can help by conducting R&D, incorporating green chemistry and engineering into their teaching, and by training students who understand the importance of environmental stewardship. And industry benefits by solving environmental challenges, thereby, allowing better focus on its core business issues.

The *Vision 2020* report outlines several steps to meeting its goals of maintaining the industry's competitive advantage into the next century. Those that are relevant to this conference include generating and use of new knowledge, and creating momentum for partnership. The study group concluded that growth and competitive advantage of the chemical industry depend upon individual and collaborative efforts of industry, government, and academe to improve the nation's R&D enterprise. Much of this week's conference focuses on the technical areas highlighted in the report by bringing an environmental focus to these issues. It is here that U.S. companies have a real competitive advantage. We lead the world in the rapidly growing business of environmental technologies. These technologies will reduce risk, enhance cost effectiveness, and improve process efficiency by creating products and using processes that are environmentally beneficial benign. By discussing the scientific and engineering advances that are needed for environmentally-sound innovation, we can help stimulate further opportunities for growth within our industry.

Tomorrow, tied to this conference is the Presidential Green Chemistry Challenge Awards. This is an excellent example of how government, academe, industry, and professional societies have joined together to recognize and contribute to the advancement of the environment through chemistry. This conference is another excellent model for partnership.

During this conference, I hope you will learn from your colleagues some state of the art, useful, ways to change the way we produce and use chemicals in order to drive us towards the goal of environmentally benign manufacturing - and to drive use towards the goals outlined in the *Vision 2020*.

At the beginning of my talk, I noted that you were involved in a growing movement to transform the way chemicals are produced. I urge you to use the knowledge that you gain at this conference about green chemistry and engineering as a base for encouraging better understanding of environmental issues and their importance to all of us as we seek innovations for a cleaner world.

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**DR. RONALD C. BRESLOW'S SPEECH  
AT THE  
1997 GREEN CHEMISTRY AND ENGINEERING CONFERENCE**

I had the pleasure last year of speaking at the first of the Green Chemistry Awards. They were, I thought, outstanding, and this year's awards are, as well, outstanding. I know this because this year I was on the committee. That's probably supposed to be privileged information.

But I think it's safe if I tell you, those of you who are winners, that I voted strongly for you. And those of you who were disappointed this year, who didn't win in spite of excellent proposals, I voted for you, too, but was overruled by the rest of the committee. I hope I have made no enemies here.

The American Chemical Society and the Environmental Protection Agency shared this year a Hammer Award, which was given by Vice President Gore to recognize initiatives that really move towards re-engineering our society in an important way. I think we received it because of our role in this green chemistry movement. We certainly are proud of the award and proud of the activities that have led to it.

I think that I mentioned last year, and let me mention again, it's a curious thing in a way to single out one



science; that is, why green chemistry? Why not, for instance, green astronomy? I think all of you in the audience know why. Because we are really a very different kind of field from many other sciences. Many sciences are fundamentally natural sciences exploring the world and trying to understand what it's about. And chemistry does that.

But chemistry has this enormous creative part of it that not every other science has, and the creative part often leads to very practical applications. As Paul Anderson pointed out, chemistry is the basis of the modern pharmaceutical industry. It's the basis, of course, of modern materials. The contributions of chemistry are absolutely enormous.

Some of the numbers that I think are interesting, have to do with the so-called chemical process industries. Chemical industry can be fairly narrowly defined, but the chemical process industries are broader. They involve every industry that uses chemistry in some way to carry out a transformation and make a product. So, for instance, the leather industries would be part of chemical process.

As an aside, I can tell you an interesting thing about the leather industries. I was in India earlier this year and visited the Central Leather Institute in India. They are undergoing a tremendous transformation. The manufacture of leather is a very important industry in India, and it's been done forever in time-honored ways involving treating the hides with heavy metals. It has been decided that that's no longer acceptable.

Almost all the leather companies are being told that they have to either get out of business or change the way they operate. So the Central Leather Research Institute is heavily involved in devising entirely new technology for the manufacture of leather using enzymatic methods to treat the hides in order to get rid of all this heavy metal pollution.

Thus it's not just in the United States that people are concerned about this. All over the world — in Japan, as well, which I've also visited — all over the world, people are very much concerned about how to do what we need to do to maintain a lifestyle that we all think is desirable and at the same time avoid the damage to the environment that can come from doing it in the wrong way.

In terms of value-added, the chemical process industry as broadly defined — that is, the chemical industry and the pharmaceutical industries, leather, rubber, petrochemicals; the whole area where people do chemistry and carry out these chemical processes — constitutes over 30 percent of the economy, the manufacturing economy. And that doesn't even include so-called primary metals.

But as you all know, gold and platinum and a few other metals exist naturally. Everything else we make. We take some stuff out of the ground and cook it up and turn it into a metal, in processes designed by chemists, monitored by chemists, operated by chemists. And that's about another four percent.

It's surprising in a way that chemical process industries are 31 percent and making iron and steel and these primary metals is only four percent. But it shouldn't surprise you because we're just much bigger than any other industry. For instance, the automotive industry, these people who take pieces of metal that's produced by a chemist, bend them around, turn them into funny shapes so we can use them. They constitute four percent of U.S. manufacturing in terms of value-added.

We are larger in terms of the contribution judged by this than any other component of the economy. In fact, the only other manufacturing sector that is even in double digits is the category called "all other." And that's ten percent. So it's a huge operation. Obviously, we don't want to close it down. And it's not surprising that it has tremendous economic impact.

But I think all of us in the field of chemistry have felt for a long time very ambivalent about the contributions that chemistry makes. We're very proud of the medicines that have, say, improved life expectancy — in 1900, the life expectancy for a U.S. male born in this country was 47 years. Now it's 74 years; a tremendous increase, better than a 50 percent increase in life expectancy.

We're very proud of these contributions. But — and there has always been a but — we wish that it could be done without damaging the environment; without causing the sort of negative effects in terms of air pollution, water pollution, pollution of the earth that I think we all have felt was not a desirable byproduct of this kind of activity.

Well, the new story is that chemistry has changed. Chemistry has understood that it is terribly important to do these good things that are so important to our society at the same time that we respect their environmental effect and do something to make sure that we don't damage the environment. Paul Anderson mentioned the *Responsible Care*® program that's been adopted by the Chemical Manufacturers Association. They make, I think, something like 90 percent of all the chemicals made in this country. And they have agreed, all signed onto this *Responsible Care*® idea, that they will do this in such a way not to cause damage. Obviously implicit in that as well is that the products will themselves be benign in every important sense.

We learned some very interesting things in the course of thinking about what to do about the environment. And one of the lessons that came to us, a very interesting lesson, is that there's such a thing as too much stability. We never thought so. We thought that if you were going to make a refrigerant, you might as well make it so that it will last for a thousand years, stick it on a shelf and maybe a thousand years from now, somebody can pull it off the shelf and use it.

Or in the case of agriculture chemicals, spray it on the fields and it will be there for 50 years doing its job. I think that we now understand that that's not desirable. It's a whole new challenge for chemistry, and a very interesting one, to get controlled lifetime for compounds so that they are stable during the time when we need them; but so that they degrade or in other ways become benign after that so that we don't have things lasting forever; so-called persistence.

Persistence we used to think was a virtue. We now recognize that it's a problem. It represents a tremendous research challenge for chemistry. A lot of you in this audience have recognized this and are addressing it with the kinds of programs that you are submitting.

I think it's fairly clear from my description of this role of chemistry, and of the importance that it plays, that I don't agree with one of our national leaders who announced that we are about to move from the age of physics to the age of biology.

Chemistry and its contribution to human welfare will continue to be, I think, one of the major sciences — I would say the major science. And certainly, it's the one that we have to pay attention to — we, in the field — and make sure that we do this in a benign way.

The argument for this was laid out quite a while ago. I'm not a Biblical scholar, but I looked around to find an early statement of the founding document of the Environmental Protection Agency. I found it in the Book of Revelations in the Bible which said, "Harm not the earth, neither the seas, nor the trees." It doesn't cover everything, obviously, but it's a pretty good start.

It's a message that we all take seriously. In the course of doing what we have to do, we have to do it in such a way as to be friendly to the environment; make it something that we can be with unmixed pride. We can look at our contributions without saying, yes, but we wish it weren't at the cost of damage to the environment.

So I think that it's a great, great activity that you are all involved in. It's also unfortunately a great untold story, this change in the major industry that has made such a huge contribution to human welfare, this change to a tremendous concern with seeing that it all be done in an environmentally friendly way. Maybe they don't like to publish good news.

For whatever reason, I just haven't read about it and I think it's a shame. We have to work not only on doing this, but on making sure that the message gets out. It's terribly important that young people, and legislators, and our fellow citizens understand that chemistry has taken a new turn, and that now there is a considerable concern with making sure that all of the contributions we make are done with full concern for the environment.

That sea of change is irreversible. It's a sweeping change throughout the industry and throughout all of our consciousness. I think it's terribly important that the story be told. So I hope that one of the things that will come out of these awards is that those of you who are winning these awards and are involved in your local media will make sure that they get this message; your contributions are important, but they are part of a sea of change in the whole way that chemistry is addressed in this country, and in the world.

Anyway, I want to congratulate the winners. I want to embolden those who didn't quite make it. They were

excellent awards. We could easily have given twice as many awards as we did, but we are limited by some rules. But please keep trying and keep sending in proposals for funding for this kind of activity, and keep sending in nominations for awards. I think that this is a building movement and you are the ones who are in the front line, making the contribution to it. Thank you very much.

1997 Green Chemistry &  
Engineering Conference

**Implementing Vision 2020 for the Environment**

June 23-25, 1997

**ENVIRONMENTALLY  
BENIGN  
SOLVENTS**



## **GREEN CHEMISTRY AND ENGINEERING A CRITICAL BUILDING BLOCK FOR SUSTAINABLE CORPORATIONS**

Dr. Paul V. Tebo

Safety, Health & Environment, E.I. duPont de Nemours & Co., Inc., Wilmington, DE

### **ABSTRACT**

DuPont will enter its third century of operation in 2002 and continue its long tradition of creating value through technology. However, the technology of the future must create products, processes, and services that are inherently safer and which have increasingly less environmental impact. DuPont, and other companies, in cooperation with universities, government research facilities, and others must, and will, provide the leadership for creating the "green" technology for sustainable growth in the 21st century.

### **THE LAST TWENTY-FIVE YEARS**

Over the past 25 years, the leadership for environmental improvement has come primarily from government agencies, like the EPA, with strong input from major environmental organizations. The vision has been primarily focused on cleaner air, cleaner water, protection of endangered species and other areas where damage has been done over a long period of time. The sense of urgency for improvement has been created by an exponential set of environmental laws and regulations. And, the result has been substantial improvement to the environment, but often at substantial cost.

### **TRANSITION**

Since the mid-1980s, we have been in a transition period to a new way to produce additional environmental improvement. Some call this the period of increasing corporate environmental stewardship or business-led environmental management. It has resulted in environmental improvement that is substantially beyond what the laws and regulations would require and, for many, at substantially less cost.

For many corporations, aggressive goals to reduce environmental impact have been set and met. These include reductions in CFCs, air toxics, air carcinogens, hazardous and non-hazardous waste, product packaging waste, and, in some cases like DuPont, a commitment to reduce greenhouse gas emissions. Along the way, the EPA and other agencies have created a series of very important voluntary programs like 33/50, WasteWi\$e, ClimateWise, Green Lights, and Project XL. In addition, several groups like the Aspen Institute, The Global Environment Management Initiative, and others have produced very thoughtful suggestions for how to change the current regulatory system in a way that will produce more environmental improvement at lower cost.

Today, many corporations are operating in a way that environmental improvements, beyond those that are required by the law, are an integral part of their strategic business plans and where many of these improvements produce substantial bottom-line benefits. In essence, proactive companies are finding the theme "good for the environment and good for business" to be credible and real.

### **THE NEXT TWENTY-FIVE YEARS**

Over the next 25 years, an increasing number of business leaders will be leading environmental improvement efforts in a way that creates a source of competitive advantage for their corporations. In addition, their vision will be one of "sustainable growth" with improvement goals set and met in at least the following areas: emission/waste reduction with a goal of ZERO; material, energy, and water-use efficiency, with very substantial use of recycled and reused materials, and renewable resources; inherently safer products, processes and distribution; reduction in total system impact through comprehensive use of life cycle assessment and "design for environment" tools; significant customer and societal value created per unit of resources extracted; and significant shareholder value created.

For companies operating in this mode, the sense of urgency will come from the enormous value to be captured, and the substantial competitive advantage to be gained, opposite those companies who only meet the minimum requirements of the laws.

### **THE ROLE OF GREEN CHEMISTRY AND ENGINEERING**

The role of "greener" technology has obviously played an enormous roll in getting us to this point, and will be even more important in the future. Examples include:

- \* very high yield, very low waste, process technology
- \* technology to create useful by-products from waste
- \* technology to reuse/recycle waste
- \* zero waste and emissions plants
- \* inherently safer processes and distribution
- \* inherently safer products and intermediates
- \* low use rate products

The presentation on June 23 will provide brief examples to illustrate several of these areas.

### DREAM OR REALITY?

Is the achievement of a truly sustainable corporation in the 21st century a vision that can become reality, or just a dream? My answer is that business success will depend on bringing this vision to reality. To do this will require visionary and inspiring leadership; unprecedented cooperation between the business sector, academia, government agencies, environmental organizations, and others; very strong support for creative and innovative approaches to both technology development and regulatory flexibility; and... opportunities, like this landmark Green Chemistry and Engineering Conference, to learn, share, and encourage each other.

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### SUPERCRITICAL FLUIDS AS SOLVENT REPLACEMENTS IN CHEMICAL SYNTHESIS

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### MOTIVATION

Opportunities exist for utilizing supercritical fluids as solvents for application to specialty chemical manufacture. In this paper, the use of supercritical fluids consisting of carbon dioxide, water, and mixtures employing solubility enhancers and cosolvents as replacements for environmentally hazardous solvents, such as toluene, methylene chloride and tetrahydrofuran (THF), will be discussed. Homogeneous and multiphase reactions and catalyzed and non-catalyzed pathways are possible. Supercritical fluids are attractive because of their potential for altering reactivity, solubility, phase stability, and thermodynamic and transport properties by controlling temperature and pressure or density in and around the critical region of the solvent. (Eckert and Chandler, 1997; Savage *et al.*, 1995; Aida, 1997; Subramanian and McHugh, 1986) Important reactivity issues that may be influenced by density and solvation effects include reaction rates, product yields, and stereo- or regio-selectivity. Because solubility can be changed significantly by changing density, the possibility for rapid and complete separations of reactants, products, and by-products exists along with the opportunity to produce controlled, solid particle morphologies in the manufacture of certain chemical products. Commercial applications of supercritical fluids as replacement solvents depends on two key engineering issues: (1) the requirement for operation at high pressures, typically 50 to 300 bar, and (2) whether reaction rates and selectivities can match or exceed those obtained in conventional liquid-phase solvents.

### REPRESENTATIVE REACTION STUDIES

Recognizing that we cannot provide an exhaustive review of reaction studies in scCO<sub>2</sub> we offer a few illustrative examples as outlined in Figure 1:

**Diels-Alder reactions** represent an important class of organic synthesis reactions that have extensive

applications in the manufacture of pharmaceuticals and speciality chemical products. Supercritical carbon dioxide has been investigated as a potential replacement for hexane, toluene, methylene chloride and other liquid hydrocarbon solvents because of its low toxicity and other positive environmental attributes (Savage, *et al.*, 1995; Kim and Johnston, 1988; Renslo, *et al.*, 1997; Weinstein, *et al.*, 1996). In our studies at MIT, we have focused on measuring rates of reactions and selectivity as a function of solution density and temperature. Two examples of Diels-Alder reactions studied in scCO<sub>2</sub> in our laboratory are shown in Figure 1: the cycloaddition of methyl acrylate and isoprene and of cyclopentadiene and ethyl acrylate. For these reactions, reaction rates and regioselectivity in scCO<sub>2</sub> remained essentially the same as under normal liquid phase synthesis where the *para* to *meta* isomer ratio was approximately 70:30 (Renslo, *et al.*, 1997). These results differ from the striking reversal of normal regiochemical behavior reported by Ikushima and co-workers (1990, 1992) which may have been caused by the presence of multiple phases in a sub-critical mixture. Second-order reaction rate constants, normalized using a fixed density of 0.5 g/cm<sup>3</sup> for the reference state at the same temperature, were correlated with solution density following a simplified Transition State Theory analysis of the effect of changing solvation conditions (Weinstein *et al.*, 1996). Figure 2 provides an empirical correlation of the normalized rate constant [ln(*k/k*<sub>0</sub>)] as a function of density ( $\rho$ ). Frequently, activation volumes are used as an empirical scaling parameter to quantify the magnitude of density/pressure effects (for example, see Johnston and Haynes, 1987).

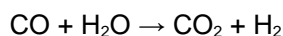
**Carboxylation reactions** are also of interest as they suggest a combined role for scCO<sub>2</sub> as a reactant and as a solvent medium. At MIT, we have begun studies of the direct carboxylation of phenol to form *para*- and *ortho*-hydroxybenzoic acid via the Kolbe-Schmitt reaction operating under supercritical conditions (see Figure 1). This reaction is a key step in the commercial synthesis of aspirin (via salicylic acid).

**Phase transfer catalysis reactions** in scCO<sub>2</sub> have been studied by Eckert and co-workers with rather interesting results (Eckert and Chandler, 1997). One example is illustrated in Figure 1 -- the nucleophilic displacement by Br<sup>-</sup> ion of the chlorine heteroatom on benzyl chloride. In this reaction study, the solubility of the phase transfer catalyst (tetraheptylammonium bromide) in scCO<sub>2</sub> was enhanced using a co-solvent (Boatright, *et al.*, 1994; Dillow, *et al.*, 1996).

**Polymerization reactions** can be effectively carried out in near critical and supercritical carbon dioxide. DeSimone and coworkers at the University of North Carolina (Kendall and DeSimone, 1997; Guan, *et al.*, 1992; DeSimone, *et al.*, 1992; Canelas, *et al.*, 1996) have investigated homogeneous, precipitation, and dispersion polymerizations of fluorinated monomers in scCO<sub>2</sub>. These reactions are particularly advantageous because of the high solubility of fluorocarbons in scCO<sub>2</sub> which facilitates the free radical polymerization of high molecular weight polymers that retain their solubility.

**Friedel-Crafts reactions** typically involve Lewis acid catalyzed pathways leading to acylation or alkylations. Tumas and coworkers at Los Alamos National Laboratory (Morgenstern, *et al.*, 1996; Birnbaum, *et al.*, 1997) have utilized scCO<sub>2</sub> as a medium to carry out aromatic acylations and alkylations using AlCl<sub>3</sub> as illustrated in Figure 1 for the acylation of naphthalene with acetyl chloride to form adduct isomers. Detailed rate and selectivity determination await further study.

**Reactions in near critical and supercritical water** are being examined for both synthesizing and destroying organic compounds using hydrolysis and oxidation pathways (Tester, *et al.*, 1997; Savage *et al.*, 1995; Kuhlmann, *et al.*, 1994; Eckert and Chandler, 1997). For example, the water-gas-shift reaction:



has been shown to proceed homogeneously in supercritical water at rates orders of magnitude greater than expected by extrapolation of low-pressure, gas-phase hydrolysis data.

Other recent investigations of using scCO<sub>2</sub> as a reaction media include studies by Tanko and Blackert (1994) and Jessop and coworkers (1995, 1996). In addition, Debenedetti and coworkers reported a modest pressure dependence of selectivity for toluene disproportionation to benzene over a zeolite catalyst near the critical point of toluene (Collins, *et al.*, 1988).

## DEVELOPMENT ISSUE

Solubility enhancers are frequently needed to facilitate high productivity and yields for processing in supercritical fluid solvents. Co-solvents (Eckert and Chandler, 1997) and molecularly designed surfactants (Harrison, *et al.*,

1996 and Johnston, *et al.*, 1996) are currently being developed to increase solubility of reactants and products in scCO<sub>2</sub>. In addition, understanding how to control solubility by adjusting temperature and pressure is vital to the design of efficient phase partitioning steps to separate products. Further, knowledge of how solvation influences reaction rates and selectivities is needed to specify optimum operating conditions. All of these requirements suggest the need for a robust research program with strong connections between the scientific (synthetic organic and physical chemistry) and the technology (chemical process engineering) components (see Figure 3).

## ACKNOWLEDGEMENTS

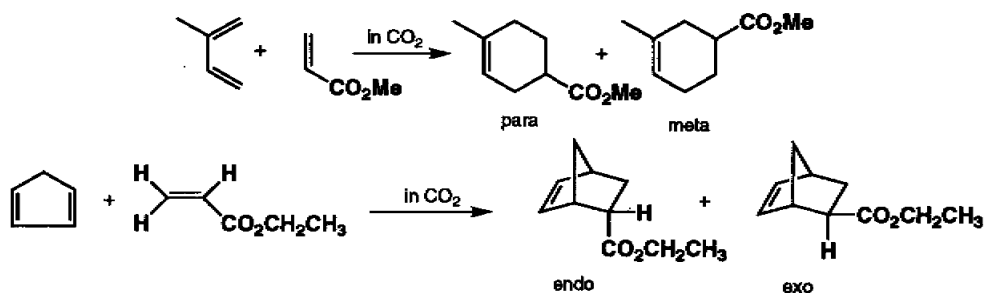
We gratefully acknowledge the support of the Emission Reduction Research Center and the Clean Harbors corporation in the early phases of our work. Prof. Jeffery Steinfeld of MIT and Dr. Paul Anastas of the EPA have provided constructive suggestions and insights. Joshua Taylor provided helpful assistance in preparing the figures.

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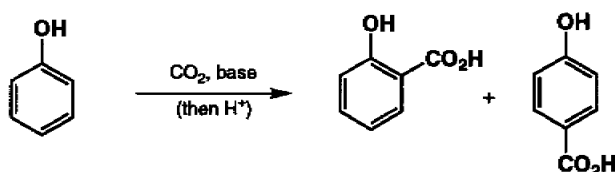
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Carbon-carbon bond formation: Diels-Alder reaction  
(examined by Tester and co-workers)

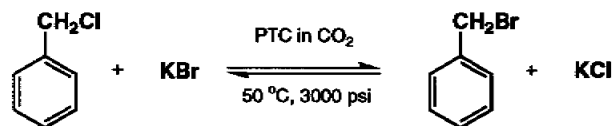


Carboxylation reaction: the Kolbe-Schmitt (Marasse modification) reaction  
(examined by Danheiser and co-workers)



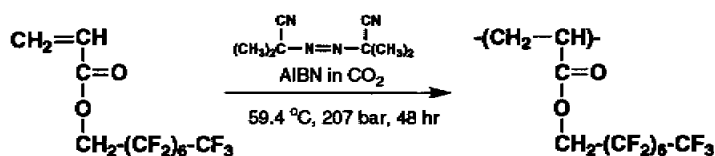
**Figure 1.** Representative model reaction systems using supercritical carbon dioxide (scCO<sub>2</sub>)

Phase Transfer Catalysis  
(examined by Eckert and co-workers)

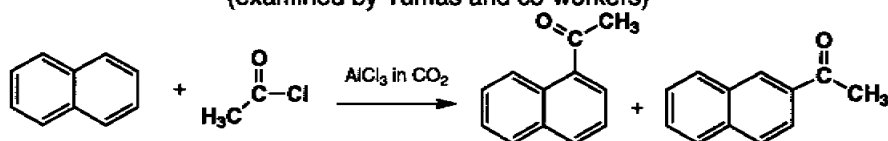


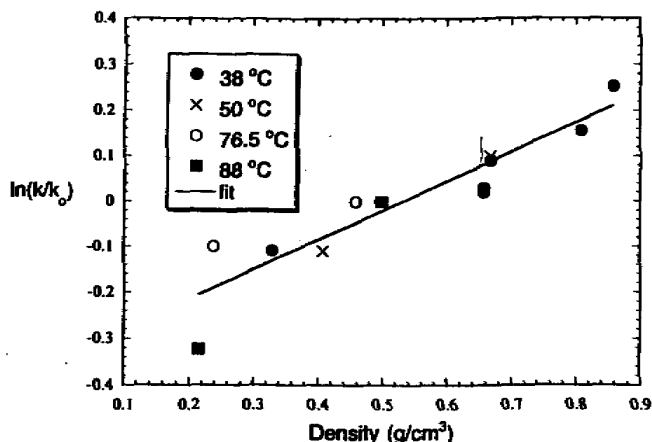
PTC = tetra-*n*-heptylammonium bromide or 18-crown-6

Polymerization  
(examined by DeSimone and co-workers)



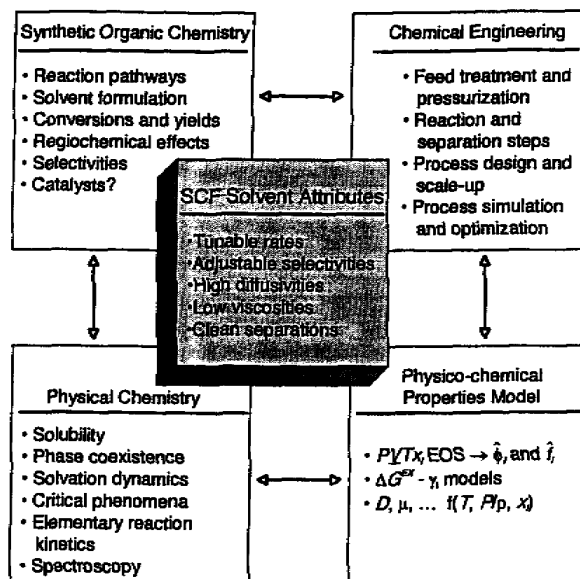
Friedel-Crafts reaction  
(examined by Tumas and co-workers)





**Figure 2.** Density dependence of the natural logarithm of the rate constant for the bimolecular Diels-Alder reaction between cyclopentadiene and ethyl acrylate in scCO<sub>2</sub> normalized to  $k_0$  at the same temperature  $T$  at a density of 0.5 g/cm<sup>3</sup> (Weinstein, *et al.*, 1996).

**Figure 3.** Supercritical solvents in organic synthesis -- linkages among synthetic organic chemistry, physical chemistry and chemical engineering.



### DENSE PHASE CARBON DIOXIDE AS AN ALTERNATIVE SOLVENT FOR CATALYTIC TRANSFORMATIONS AND SYNTHETIC CHEMISTRY

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#### Abstract

The aim of our research is to explore the potential of supercritical fluids as a reaction medium for stoichiometric and catalytic chemical transformations in an effort to develop new, environmentally-friendly methods for chemical synthesis and processing. This approach offers the possibility of opening up substantially different chemical pathways, increasing selectivity at higher reaction rates, facilitating downstream separations and mitigating the need for hazardous solvents. We have found that supercritical fluids, particularly CO<sub>2</sub>, are an effective solvent for a wide range of chemical reactions including: asymmetric catalytic hydrogenation and hydrogen transfer reduction; selective catalytic oxidation of olefins using a number of transition metal catalysts; carbon-carbon bond forming reactions including Heck coupling and Lewis acid catalyzed alkylations and acylations; and several processes that utilize carbon dioxide as both a reagent and solvent.

## Introduction

The use of supercritical fluids as reaction media offers the opportunity to replace conventional hazardous organic solvents and also to optimize and potentially control the effect of solvent on reactions. An advantage of supercritical fluids is that several important solvent properties can be "pressure-tuned" from gas-like to liquid-like, providing opportunities for improved chemistry. Supercritical fluids can have liquid-like densities and solvent strength which can be "tuned" by adjusting the density of the medium allowing for control of the solute solubility along with density-dependent properties such as dielectric, viscosity, and diffusivity with pressure control. Simple solubility control through pressure could also allow facile separation of products and catalysts from the solvent.

Supercritical fluids also share many of the advantages of gases including miscibility with other gases, low viscosities, and high diffusivities, thereby providing enhanced heat transfer and the potential for faster reactions, particularly for diffusion-controlled reactions involving gaseous reagents such as hydrogen or oxygen. Carbon dioxide ( $T_c = -31.1\text{ }^\circ\text{C}$ ,  $P_c = 7.3\text{ MPa}$ ) has the further advantages of being nontoxic, nonflammable, inexpensive and unregulated. Its electrophilic nature and the fact that it cannot be further oxidized makes  $\text{CO}_2$  an ideal solvent for carrying out both electrophilic and oxidation catalysis. The enhanced thermal conductivity of supercritical  $\text{CO}_2$  (SC  $\text{CO}_2$ ) relative to organic solvents, coupled with its stability towards oxidation suggests that it can act as an efficient solvent for buffering heat transfer, even for highly exothermic reactions.

The focus of our research in supercritical fluids is to explore the potential for solvent replacement by understanding chemical reactivity in this medium. In addition, we are seeking enhanced selectivity and reactivity as well as new chemistry in supercritical fluids. Our approach has been to explore several fundamental and industrially important catalytic processes in supercritical fluids in order to understand their potential to benefit from the advantages of supercritical fluids as reaction media. In our view, the most promising reactions are those that: 1) work well in nonpolar solvents such as hexane or halocarbons, 2) are solvent-sensitive (and this likely to be "pressure-tunable"), 3) lead to high-value products (mitigating the capital investment barriers to implementation of new technology), or 4) utilize gaseous reagents which are not highly soluble in conventional solvents, e.g. hydrogen or oxygen.

We have studied several known catalytic processes and compared rates and selectivities in supercritical fluids to those in conventional organic solvents. Specifically, we have investigated the following catalytic processes:

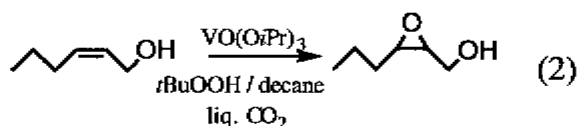
- dihydroxylation or cleavage of olefins by Ru and Os phase transfer catalysts
- vanadium and titanium-catalyzed epoxidation of allylic and homoallylic alcohols
- iron-porphyrin catalyzed oxidation of cyclo-hexene
- cobalt-catalyzed ring-opening of cyclohexane to adipic acid
- rhodium and ruthenium catalyzed asymmetric hydrogenation/reduction of olefins
- Lewis acid catalyzed acylations and alkylations
- palladium-catalyzed Heck coupling of aryl halides and olefins
- use of  $\text{CO}_2$  as a solvent and reagent for isocyanate synthesis and epoxide ringopening polymerization

## Summary

### Selective Oxidation Catalysis

A number of oxidation catalysts have been examined in supercritical  $\text{CO}_2$  in our laboratory. These can be divided into three categories: phasetransfer carbon-carbon double bond cleavage using  $\text{RuO}_4$  or  $\text{OSO}_4$  in water/ $\text{CO}_2$  mixtures; epoxidation of olefins via oxo-transfer from high-valent titanium and vanadium complexes using hydroperoxides; and air-oxidation of cyclohexene and cyclohexane using highly fluorinated iron porphyrins and cobalt catalysts, respectively.

We have used a number of vanadium catalysts ( $\text{V}_2\text{O}_5$ ,  $\text{VO}(\text{acac})_2$ ,  $\text{VO}(\text{OR})_3$ ) to mediate the t-butylhydroperoxide epoxidation of allylic and homoallylic alcohols in supercritical and liquid  $\text{CO}_2$ .



A large number of substrates can be selectively epoxidized in this environmentally benign solvent. In addition, we have shown, for the first time, that high enantioselectivities can be achieved for epoxidations in liquid  $\text{CO}_2$  using chiral auxiliary ligands on vanadium or titanium. This work also reveals that liquid  $\text{CO}_2$  could be an effective solvent for a

number of catalytic transformations even at relatively low temperatures (below 0 °C).

### Asymmetric Catalytic Hydrogenation

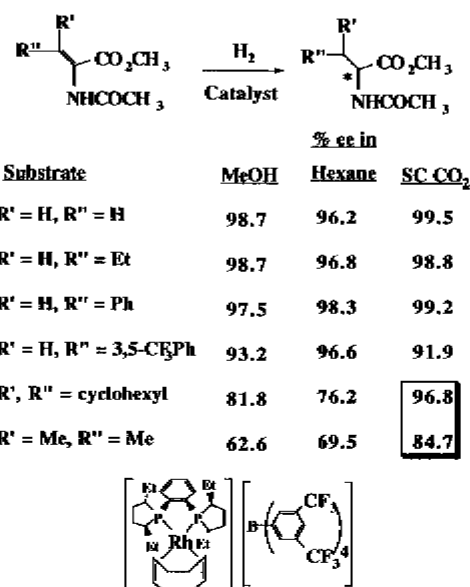
The design of stereoselective reactions that provide only one of two possible product enantiomers remains a primary goal of modern organic and organometallic chemistry. Asymmetric catalysis, which involves the use of chiral transition metal or main group complexes, has emerged as one of the most powerful, cost-effective methods for the generation of a wide variety of enantiomerically enriched compounds. Asymmetric catalytic hydrogenation of prochiral olefins and carbonyl compounds constitutes one of the key methods for introducing chirality into a wide range of molecular frameworks including pharmaceutical and agrochemical precursors. The asymmetric catalytic hydrogenation of  $\alpha$ -enamides in SC CO<sub>2</sub> can lead to enantioselectivities equal or superior to those observed in conventional organic solvents.

Our work has focused on rhodium and ruthenium catalysts containing chiral biphosphine ligands, 1,2-bis(trans-2,5-diethylphospholano)benzene (DuPHOS) or 2,2'-bis(diphenyl-phosphino)-1,1'-binaphthyl (BINAP).

The cationic rhodium catalysts can be made soluble in supercritical CO<sub>2</sub> by using the highly lipophilic anion (tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate (B(ArF)<sub>4</sub><sup>-</sup>) as the counterion. The ability to solubilize cationic catalysts has broad implications for catalysis in supercritical fluids.

The reduction of enamides with the Rh-DuPHOS catalyst proceeds cleanly and completely in SC CO<sub>2</sub> to provide the  $\alpha$ -amino acid derivatives (parent enamide in Eqn. 5) with high enantioselectivity (90.9-99.7 % ee). Significantly, the results in Table 1 clearly indicate that enantioselectivities achieved with this catalyst system in supercritical CO<sub>2</sub> are very high, and are comparable to those achieved in conventional solvents.

Particularly striking examples are the reduction of b,b-disubstituted  $\alpha$ -enamides that give significantly higher ee's in SC CO<sub>2</sub> relative to hexane or methanol (Table 1).



**Table 1.** Enantioselectivities for enamide hydrogenation.

The hydrogenation reaction is quite general and over 30 substrates (enamides, hydrazones, enol acetates) have been reduced in SC CO<sub>2</sub> using the DuPhos-Rh complexes resulting in enantioselectivities that are equal or superior to conventional solvents.

### Asymmetric Hydrogen Transfer Reduction

The BINAP-Ru catalysts described above also lead to high enantioselectivities for the hydrogen transfer reduction of olefins using formic acid and triethylamine in SC CO<sub>2</sub>. The  $\alpha$ -enamides can be reduced cleanly under these conditions to afford the corresponding amino acid derivatives with high enantioselectivities. These hydrogen transfer reductions do not exhibit any solvent effect and no significant pressure effects were observed. These enantioselectivities, particularly those observed for the esters, are, however, among the highest yet reported for hydrogen transfer reduction of  $\alpha$ -enamide substrates.

### Carbon-Carbon Bond Formation

We have recently investigated palladium-catalyzed carbon-carbon bond forming reactions in supercritical CO<sub>2</sub>. A number of phosphine ligands, including highly fluorinated systems, have been used in the Heck reaction with a number of substrates. The Stille coupling of various substrates with palladium catalysts has also been studied. Both classes of reactions have been shown to proceed in CO<sub>2</sub> and we are currently studying the effects of substrate, ligands, and pressure on the rates and selectivities of these reactions.

### Conclusion

Our work has demonstrated that dense phase carbon dioxide can be used for a wide range of catalytic

processes, including reduction, oxidation and carbon-carbon bond formation. In several cases, particularly asymmetric hydrogenation, we have observed enhanced selectivities without compromising reactivity. In addition to exploring other catalytic processes, it is clear that there are exciting opportunities for research other aspects of chemical processing in supercritical fluids including the development of separations technology, catalyst recovery, phase behavior and modeling, and new reactor concepts.

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# **SUPERCRITICAL FLUIDS**



## MEASUREMENT, MODELING AND COMPUTATION OF THE PHASE BEHAVIOR OF CO<sub>2</sub>-BASED REACTION SYSTEMS

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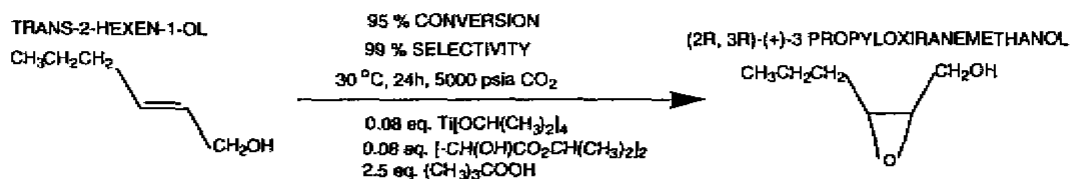
### ABSTRACT

An important consideration in using CO<sub>2</sub> as an environmentally benign solvent to replace hazardous organic compounds in reactions is the phase behavior. We have used a two pronged approach to address this issue. First, we present phase equilibrium measurements and modeling of components in the allylic epoxidation of *trans*-2-hexen-1-ol (alcohol) to (2R,3R)-(+)-3-propyloxiranemethanol (epoxy), which occurs with very high enantiomeric selectivity in CO<sub>2</sub>. We have investigated the high pressure phase behavior of the components in this reaction with CO<sub>2</sub> at temperatures between 303.15 and 323.15 K and pressures between 31.5 and 110.2 bar. The components include *trans*-2-Hexen-1-ol, (2R,3R)-(+)-3-Propyloxiranemethanol, Diisopropyl L-tartrate, Titanium (IV) isopropoxide, *tert*-Butyl hydroperoxide, and *tert*-Butyl alcohol. Modeling with the Peng Robinson equation of state gave reasonably good results for the two phase (vapor-liquid equilibrium) regions of all systems and did successfully predict three phase regions for both binaries that exhibited VLE, but generally at conditions different than those observed experimentally. Second, we have developed a computational technique based on interval Newton generalized bisection method that is completely reliable for the determination of phase stability. We have implemented this technique for the general cubic equations of state that we use to model high pressure phase behavior.

### INTRODUCTION

High pressure gases and supercritical fluids can be used to replace traditional organic solvents in industrially important reactions. Supercritical carbon dioxide (CO<sub>2</sub>) is particularly attractive as an environmentally benign solvent and numerous reactions have been done successfully in liquid and supercritical CO<sub>2</sub>, sometimes with rates and selectivities as good as or better than can be achieved in conventional liquids.<sup>1,2</sup> There is also the possibility that the solvent properties of CO<sub>2</sub> could be used to facilitate both the reaction and separation stages of the overall process. However, the solubility of many compounds is rather low in CO<sub>2</sub> and high pressures may be necessary to achieve reasonable concentrations or a one phase mixture, if that is necessary. Therefore being able to measure, model and accurately predict the high pressure phase behavior of CO<sub>2</sub> based reaction systems is important to the ultimate design and implementation of CO<sub>2</sub> as a replacement solvent in reactions.

Our general program to deal with this problem has been 1) to have available experimental methods to take the limited amount of phase equilibrium data that is needed to fit parameters in thermodynamic models, 2) to develop new general methods to reliably perform phase equilibrium computations, and 3) to choose a specific system of potential interest upon which to demonstrate the experimental and new computational techniques. In this paper, we report on the phase equilibrium measurements and modeling for a specific system, the allylic epoxidation of *trans*-2-hexen-1-ol (alcohol) to (2R,3R)-(+)-3-propyloxiranemethanol (epoxy). Traditionally, this important synthesis reaction has been performed in organic solvents but it also has been done in liquid CO<sub>2</sub> at 30°C.<sup>3</sup> The reaction consists of the addition of an oxygen atom to the double ring of the alcohol (epoxidation), as shown in Figure 1. The result is two stereochemical centers formed with high enantiomeric selectivity. Our objective is to present new data on the high pressure phase behavior of binary systems of carbon dioxide with the various components in the reaction, including temperatures similar to those used by Tumas and coworkers in their study of the feasibility and selectivity of this reaction in CO<sub>2</sub>.<sup>3</sup> We will present liquid phase compositions, as well as identify the regions where three phase equilibria exist. In addition, we present modeling results of the binary systems using the Peng-Robinson equation of state (PREOS). Also, we give a brief description of the new computational techniques that we have developed to perform phase stability calculations.



**Figure 1.**  
Titanium  
catalyzed  
epoxidation  
reaction.



## EXPERIMENTAL METHODS

Phase equilibrium measurements were carried out using the static measurement apparatus, which has been described previously.<sup>4</sup> The liquid is loaded into a cell that can be observed visually and CO<sub>2</sub> carefully metered into the system. The liquid phase compositions were determined by stoichiometry, assuming that the gas phase was composed of only CO<sub>2</sub>.<sup>5,6</sup>

## MODELING

The Peng-Robinson equation of state was used to model the phase behavior of all the binaries systems, with conventional van der Waals mixing rules.<sup>7-9</sup> For each binary, one temperature independent binary interaction parameter,  $k_{ij}$ , was fit to the experimental liquid phase composition data [ $a_{ij} = (a_{ii} a_{jj})^{0.5} (1 - k_{ij})$ ]. Since the critical properties of most of the constituents were not available, they were estimated using the contribution method by Joback.<sup>8</sup> Vapor pressures were estimated using the Riedel method.<sup>8</sup> The values of the properties used in the modeling of the various binaries are given in Table 1.

**Table 1.** Properties of Components

Component Name	Formula	T <sub>c</sub> (K)	P <sub>c</sub> (bar)	$\omega$	k <sub>ij</sub>
<i>trans</i> -2-Hexen-1-ol	C <sub>6</sub> H <sub>12</sub> O	601.76	36.73	0.724	0.084
(2R,3R)-(+)-3-Propyloxirane-methanol	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	631.77	38.39	0.794	0.043
Diisopropyl L-tartrate	[-CH(OH)CO <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	691.18	30.73	0.491	0.052
Titanium (TV) isopropoxide	Ti[OCH(CH <sub>3</sub> ) <sub>2</sub> ] <sub>4</sub>	661.35	16.22	0.685	0.087
<i>tert</i> -Butyl hydroperoxide	(CH <sub>3</sub> ) <sub>3</sub> COOH	505.16	40.42	0.303	0.199
<i>tert</i> -Butyl alcohol	(CH <sub>3</sub> ) <sub>3</sub> COH	506.21	39.73	0.611	0.108

The two phase compositions were determined using the Michelsen algorithm, as implemented in LNGFLASH, which is part of the IVC-SEP Program Package.<sup>10</sup> Although this code is extremely reliable, it did fail to give the correct answer to some points close to the LLV line, thus, emphasizing the need for the new computational techniques described below.

## INTERVAL NEWTON GENERALIZED BISECTION

The determination of phase stability and ultimately phase equilibrium is a very difficult computational problem for which conventional techniques often fail by converging to a trivial or incorrect solution corresponding to a local rather than global minimum in the Gibbs energy. Thus there has been much recent interest in developing more reliable solution methods. The only method available to date which can mathematically guarantee a correct solution in connection with cubic equation of state models of interest here is a technique that we have developed<sup>11-13</sup> based on an interval Newton/generalized bisection algorithm. This approach provides the power to find with confidence all solutions to a system of nonlinear equations, and to find with total reliability the global minimum of a nonlinear objective function, provided only that upper and lower bounds are available for all variables. The technique is initialization independent and can be used in connection with any activity coefficient model or equation of state model for computing the Gibbs energy.

## EXPERIMENTAL RESULTS

The high pressure vapor/liquid and vapor/liquid/liquid equilibria were measured for six different binary systems involved in the epoxidation reaction shown in Figure 1. The range of temperatures, pressures and mole fractions for each system are summarized below:

### *trans*-2-Hexen-1-ol --- CO<sub>2</sub>

Liquid phase compositions for this system were measured at 303.15, 305.95, 313.15 and 323.15 K and pressures between 14.6 and 100.3 bar and are shown, along with compositions estimated with the PREOS, in Figure 2. This system exhibits a liquid-liquid-vapor region (LLV) which extends from 310.9 K and 79.5 bar (LCST) to 315.3 K and 86.7 bar (type-k point). The compositions of both of the liquid phases at conditions where LLV existed were rich in CO<sub>2</sub>, with typical values of about 0.8 and 0.95 mole fraction CO<sub>2</sub>.

### (2R,3R)-(+)-3-Propyloxiranemethanol ---CO<sub>2</sub>

Liquid phase compositions for this system were measured at 305.95, 313.15 and 323.15 K and pressures between 31.5 and 110.2 bar and are plotted, along with compositions estimated with the PREOS, as pressure versus composition (Pxy) in Figure 3. A LLV region was found for this binary systems, as well, and extends from 315.1 K and 86.1 bar (type-k point) to below 293.7 K and 55.8 bar, which was the lowest temperature measured. The LLV experimental liquid phase compositions were about 0.77 and 0.93 mole fraction CO<sub>2</sub> and were fairly

insensitive to pressure over the range investigated.

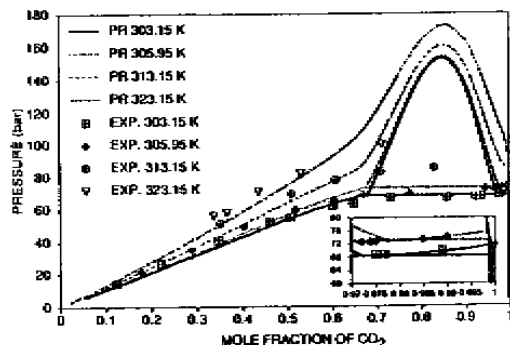


Figure 2. P-x diagram for *trans*-2-hexen-1-ol --- CO<sub>2</sub>

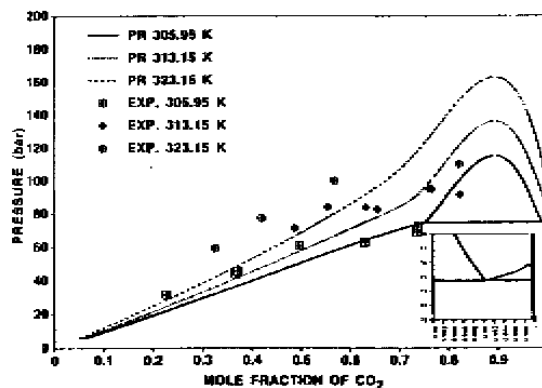


Figure 3. P-x diagram for (2R,3R)-(+)-3-propyloxiranemethanol ---CO<sub>2</sub>.

#### Diisopropyl L-tartrate ---CO<sub>2</sub>

Liquid phase compositions for this system were measured at 305.95 and 313.15 K and pressures between 46.6 and 87.2 bar. The compositions ranged from 0.50 to 0.97 mole fraction CO<sub>2</sub>. Only two-phase VLE was observed experimentally and this was what was predicted by the PREOS except at 313.15K and pressures above 87 bar, where the PREOS predicted a single phase system.

#### Titanium (IV) isopropoxide ---CO<sub>2</sub>

Liquid phase compositions for this system were measured at 305.95 and 313.15 K and pressures between 42.8 and 84.7 bar. The compositions ranged from 0.43 to 0.97 mole fraction CO<sub>2</sub>. Although only two-phase VLE was observed experimentally, the PREOS predicted two liquid phases at 305.95 at all pressures and at 313.15 at pressures up to 84.1 bar.

#### tert-Butyl hydroperoxide ---CO<sub>2</sub>

Liquid phase compositions for this system were measured at 305.95 and 313.15 K and pressures between 56.3 and 79.6 bar. The compositions ranged from 0.38 to 0.85 mole fraction CO<sub>2</sub>. Only two-phase VLE was observed experimentally and this was what was predicted by the PREOS at 313.15 K. However for 305.95 K the PREOS predicted the presence of two liquid phases.

#### tert-Butyl alcohol ---CO<sub>2</sub>

Liquid phase compositions for this system were measured at 305.95 and 313.15 K and pressures between 40.5 and 75.7 bar. The compositions ranged from 0.34 to 0.89 mole fraction CO<sub>2</sub>. Only two-phase VLE was observed experimentally and this was what was predicted by the PREOS.

### COMPUTATIONAL RESULTS

An enhanced version of our original interval Newton/generalized bisection technique for cubic equations of state models<sup>12,13</sup> is currently being developed. The enhancements are based on obtaining tighter bounds on function ranges than possible when using ordinary interval arithmetic, thus providing significant improvements in computational efficiency. The new technique has been applied to phase stability computations for several binary and ternary systems using the Peng Robinson and SRK EOS models. In all cases the correct solution to the problem was obtained. The technique also proved to be quite efficient, with solution times ranging from about 5 to 0.1 seconds (on a Sun Ultra 1/170 workstation) over a wide variety of problems.

### SUMMARY

We have presented phase equilibrium measurements for the binary components in the allylic epoxidation of *trans*-2-hexen-1-ol to (2R,3R)-(+)-3-propyloxiranemethanol in CO<sub>2</sub> and modeled the data with the PREOS. We have also developed a new completely reliable interval Newton/generalized bisection technique to perform phase stability computations for high pressure systems using any of a variety of EOS models. Future work will include prediction of the multicomponent phase behavior using the interaction parameters determined from the binary systems and comparison with multicomponent phase measurements. To perform the high pressure phase

equilibrium computations we will use the newly develop IN/GB technique. This work is important because it develops techniques and procedures to identify and reliably predict appropriate operating conditions where reactant, product and catalyst solubilities are sufficiently high in CO<sub>2</sub> to make the use of CO<sub>2</sub> as an environmentally benign replacement solvent a viable alternative.

## ACKNOWLEDGMENTS

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## NEARCRITICAL WATER FOR ENVIRONMENTALLY BENIGN CHEMICAL PROCESSING

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## Abstract

We report successful alkylation reactions in nearcritical water in the absence of added acid catalysts. Water has a strong tendency to ionize as the temperature is increased, allowing water in the nearcritical region (250-350°C) to act as an effective acid catalyst. By simultaneously employing nearcritical water as the reaction solvent and catalyst, the need for environmentally hazardous organic solvents and acid catalysts is eliminated. The high hydronium ion content of nearcritical water proved to be sufficient to synthesize a variety of substituted phenols with tertiary, secondary, and even primary alcohols. The reaction products for each of these reactions are reported.

## Introduction

Water ( $T_c = 374^\circ\text{C}$ ,  $P_c = 221$  bar) is an inexpensive and environmentally acceptable solvent that offers tremendous opportunities for pollution prevention for a wide variety of chemical reactions. The specific reactions studied in this work are typically acid catalyzed Friedel-Crafts alkylation reactions. Friedel-Crafts chemistry has been used extensively in various commercial processes such as the production of high-octane gasoline, synthetic rubber, plastics, and detergents. Furthermore, Friedel-Crafts chemistry involves electrophilic aromatic substitution and carbocation formation which are of great theoretical interest (Roberts and Khalaf, 1984). In this

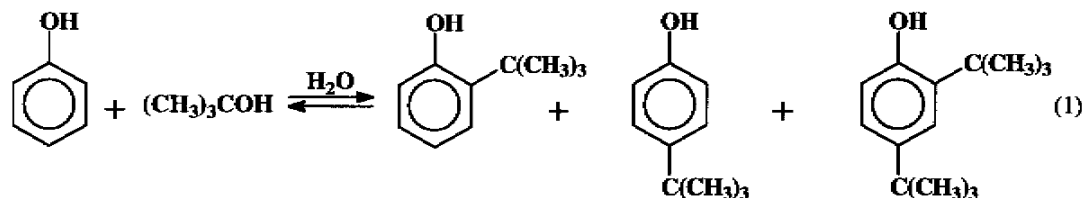
investigation, phenol and cresol were alkylated with primary, secondary, and tertiary alcohols in proton rich nearcritical water (275°C) in the absence of added acid catalysts. These alkylation reactions provide a variety of sterically hindered phenols used extensively as effective antioxidant additives during fabrication, storage, processing, and end-use of many polymer systems (Pospisil, 1988). The advantages of synthesizing the sterically hindered phenols in nearcritical water include replacement of environmentally undesirable organic solvents, replacement of environmentally undesirable acid catalysts, possible reduction of unwanted byproducts, and easier recycling of used materials.

Water is a unique solvent; its chemical and physical properties vary considerably at high temperatures and pressures when compared, to water at ambient conditions. At 300°C the density and dielectric constant of water approach those of ambient acetone (Pitzer, 1983; Kuhlmann et al., 1994), making the solubilizing properties of water similar to those of polar organic solvents at ambient temperature (Connolly, 1996; Shaw et al., 1991).

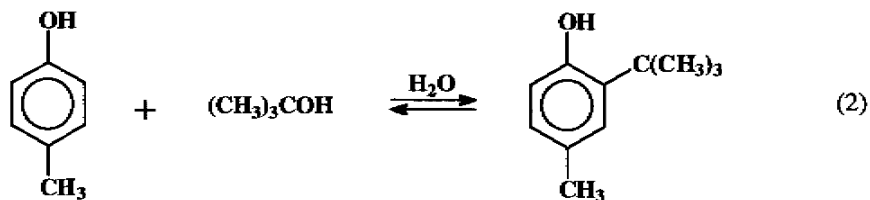
Nearcritical water also has a strong tendency to ionize, and thus is a source of hydronium and hydroxide ions far better than ambient water or acetone. The dissociation constant increases by more than three orders of magnitude when going from ambient to nearcritical conditions (Marshall and Franck, 1981), which allows water in the nearcritical region to act as an effective acid or base catalyst (Kuhlmann et al., 1994; Katritzky et al., 1996). A considerable problem with running typical Friedel-Crafts alkylations is that the reactions often require strong Lewis acids or protic acids. By employing nearcritical water to replace the required acid catalyst, the need for base neutralization, catalyst regeneration, and disposal of salt byproducts is eliminated.

### Results and Discussion

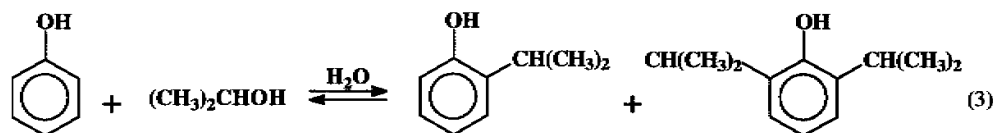
The reaction of phenol with *tert*-butyl alcohol (1) was attempted with no added acid catalyst. The high hydronium ion content of water at 275°C proved to be sufficient to allow the electrophilic aromatic substitution on phenol by *tert*-butyl alcohol. Two main reaction products were identified including 2-*tert*-butylphenol and 4-*tert*-butylphenol. The molar concentration of 2-*tert*-butylphenol reached a maximum of 17% at a reaction time of 30 hours and then began to drop off at longer reaction times to an equilibrium concentration of around 10%. On the other hand, the 4-*tert*-butylphenol appeared to increase monotonically to an equilibrium concentration of around 20%. Also, a small amount (<5%) of the di substituted product, 2,4-di-*tert*-butylphenol, was formed.



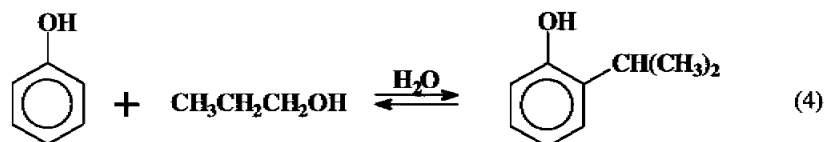
The reaction of *p*-cresol with *tert*-butyl alcohol was also attempted (2). The reaction of *tert*-butyl alcohol and *p*-cresol proceeds at a much faster rate than the reaction of *tert*-butyl alcohol and phenol. After only 1 hour, the reaction appeared to be very close to equilibrium. The only reaction product identified for this reaction was 2-*tert*-butyl-4-methylphenol, at an equilibrium concentration of approximately 20%.



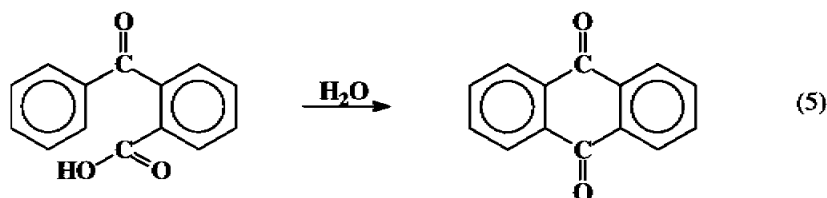
Once it had been demonstrated that the high hydronium ion content of nearcritical water at 275°C was sufficient to promote the alkylation reaction of phenol with a tertiary alcohol, the alkylation of phenol with a secondary alcohol, *iso*-propanol, was attempted (3). The reaction occurred slowly throughout a 120 hour reaction time, and the major products were 2-*iso*-propylphenol (25%) and 2,6-di-*iso*-propylphenol (10%). 4-*iso*-propylphenol was also produced but was always at a molar yield of 1 % or less.



The alkylation of phenol with a primary alcohol, *n*-propanol, was also attempted (4). As expected, the total product yields were much lower than in the previous reactions using tertiary and secondary alcohols. Throughout an entire 144 hour reaction period, the total product yield remained less than 5%, and the major product was 2-*iso*-propylphenol. It did appear that 2,6-di-*iso*-propylphenol and unrearranged 2-*n*-propylphenol were also formed but only in very low concentrations (<1 %).



In addition to the alkylation reactions described in this work, the self acylation reaction of benzoylbenzoic acid to form anthraquinone (5) was also attempted in nearcritical water at 275°C. Anthraquinone is a valuable catalyst in the bleaching process for paper production and is an important raw material for the dye industry (Bram et al., 1991). The cyclization of benzoylbenzoic acid was unsuccessful after 20 hours when no acid was added to the nearcritical water. However, at the same reaction conditions, anthraquinone was identified as a reaction product (<5% yield) when either H<sub>2</sub>SO<sub>4</sub> or HCl was employed as a catalyst. H<sub>2</sub>SO<sub>4</sub> appeared to be the more effective acid catalyst for this reaction.



## Conclusions

Phenol and *p*-cresol were effectively alkylated with tertiary and secondary alcohols, and to a lesser extent with a primary alcohol in nearcritical water. The ability of water to carry out and catalyze alkylation reactions is due to the unique properties of water (density, dielectric constant, dissociation constant) in the nearcritical region. The most important advantages of performing alkylation reactions using water as the reaction solvent are relatively low cost, replacement of environmentally undesirable organic solvents, and replacement of environmentally undesirable acid catalysts. Furthermore, by eliminating the acid catalyst, the need for base neutralization, catalyst regeneration, and disposal of salt byproducts is also eliminated.

## Acknowledgment

We greatly appreciate the financial support of Hoechst Celanese Corporation, E.I. Du Pont de Nemours, the National Science Foundation (Grant No. CTS-9613063), and the Environmental Protection Agency (Grant No. R825325).

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## SUPERCRITICAL CARBON DIOXIDE AS AN ALTERNATIVE SOLVENT FOR POLLUTION PREVENTION

Beth Fletcher, Mitra Sadeghipour, and J. M. Tanko

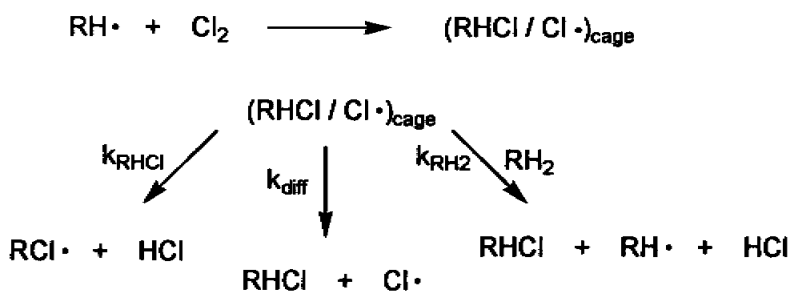
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Supercritical carbon dioxide is proving to be a suitable "environmentally benign" solvent for radical reactions, providing a unique alternative to many conventional solvents which are carcinogenic and/or damaging to the environment.<sup>1</sup> Our recent work in this area deals with two issues:

### IMPLICATIONS ASSOCIATED WITH THE USE OF SC-CO<sub>2</sub> IN TERMS OF ISSUES PERTAINING TO CHEMICAL REACTIVITY

The free radical chlorination of various hydrocarbons was examined in conventional and supercritical carbon dioxide (SC-CO<sub>2</sub>) in order to investigate variations in the chlorine atom cage effect, product distribution, and selectivity which might be attributable to unique solvent behavior in SC-CO<sub>2</sub>.

The chlorination of cyclohexane was examined in order to probe for variations in the chlorine atom cage effect (Scheme 1) due to solvent "clustering", especially at pressures near the critical pressure of CO<sub>2</sub>. The results show that the extent of the cage effect observed for this system in SC-CO<sub>2</sub> is readily predicted from extrapolations of conventional solution data suggesting no distortion of the cage effect in SC-CO<sub>2</sub>.<sup>2</sup>



Scheme 1

To examine the variations of product distribution in SC-CO<sub>2</sub>, neopentane was chlorinated in conventional and SC-CO<sub>2</sub>, as well as in the gas phase. The results show that at low pressures, the solvent cage effect becomes less important and the ratio of the 1,3- to 1,1-isomers approaches that recorded for the gas phase (where encounter of neopentyl chloride and Cl• is diffusive). In solution, the solvent plays an important role, as it effectively maintains close proximity of the neopentyl chloride and Cl•, resulting in a second hydrogen abstraction at the closest reactive site. Further, the 1,3- isomer becomes more important as viscosity is increased.

The chlorination of 2,3-dimethylbutane and propane in conventional and SC-CO<sub>2</sub> solvents afforded the potential to monitor the chlorine atom selectivity over a broad range of viscosities. However, due to substantial polychloride formation even at low pressures, the relative selectivity of tertiary to primary hydrogen abstraction reported is, at best, a general trend of the variation in selectivity with viscosity. As the viscosity of the SC-CO<sub>2</sub> increased, the selectivity decreased and approached conventional solvent values at high pressures. Chlorination

of propane resulted without any polychloride formation observed. Thus, the reported relative selectivity of secondary to primary hydrogen abstraction provides true chlorine atom selectivity values. However, these initial reactions, which covered a small pressure region, do not allow for any correlation of selectivity with pressure.

These findings demonstrate the potential utility of SC-CO<sub>2</sub> as a versatile and tunable medium for achieving desired product distributions and selectivities in high yields for free radical chlorination reactions.

#### DEVELOPMENT OF NEW SYNTHETIC METHODS AMENABLE TO SC-CO<sub>2</sub> SOLVENT

We have developed a new synthetic pathway utilizing an allyl transfer reaction and bromine atom chemistry (Scheme 2). In this process, bromine atom abstracts a hydrogen from an alkylaromatic. The resulting benzyl radical subsequently adds to the allylbromide.  $\beta$ -Cleavage of the resulting adduct radical regenerates Br• and yields the final product.

The reaction of toluene and cumene with different substituted allyl bromides have been studied. The relative reactivity of benzylic radical addition to the double bond of allylbromide is similar to the rate of addition of benzylic radical to substituted olefins. The results of chain length experiments showed that the product competes with allylbromide in the radical addition step. Selectivity experiments provide evidence for Br• as a chain carrier.

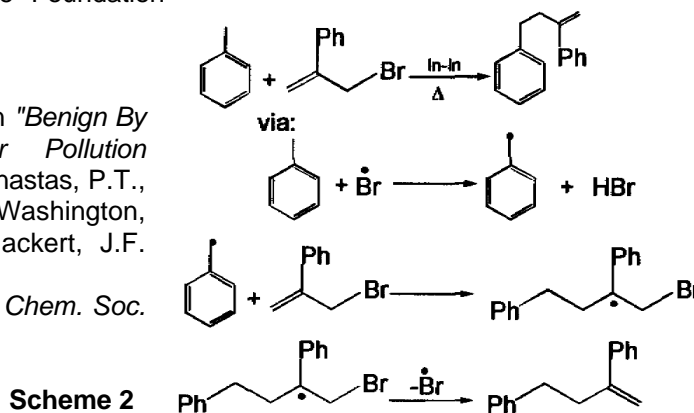
This procedure avoids the use of high reactivity species (alkylolithiums, etc.) which are frequently used in C-C bond forming reactions. Although thus far these reactions have been conducted in conventional organic solvents, we are confident that this chemistry will be amenable to SC-CO<sub>2</sub> solvent.

#### Acknowledgement.

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# AQUEOUS SYSTEMS



## WATER AS SOLVENT FOR ORGANIC AND MATERIAL SYNTHESES

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### Introduction

The use of a large amount organic solvent for various chemical syntheses leads to both resource depletion and environmental emissions. On the other hand, water is a clean, non-toxic, non-explosive, and the most abundant solvent on earth; the use of water as solvent provides opportunities of resource conservation and reduction in environmental emission, as well as a means for exploring novel synthetic methodologies. It is only within the last decade or so that people have again focused their attention on carrying out organic reactions in water. This resurgence is in large part due to the study by Breslow on the Diels-Alder reaction as well as the drive for the development of more environmentally safe chemical processes.<sup>1</sup> Many organic reactions which are traditionally carried out exclusively in organic solvents.<sup>2</sup> Thus, basic research on aqueous organic reactions lays the foundation for the development of environmentally friendly synthetic processes. This talk discusses some recent studies in our own laboratory on the use of water as solvent for both organic and material syntheses. In most cases, the studies have the dual advantages of being aqueous and being "atom economical."

### Indium Mediated Bisallylation of Carbonyl Compounds

Metal mediated Barbier-type reactions in aqueous media have shown considerable potential in organic synthesis. The use of aqueous medium for Barbier-Grignard type reactions offers numerous advantages. There is the practical convenience of not having to handle flammable and anhydrous organic solvents. The tedious protection-deprotection processes for certain acidic-hydrogen containing functional groups can be avoided, which contributes to an overall synthetic efficiency. Water-soluble compounds, such as carbohydrates, can be reacted directly without the need of derivatization. Such processes also reduce the burden of solvent disposal and its impact upon the environment. Because of its low first ionization potential, indium has been shown to be particularly effective as a mediator for such reactions.<sup>3</sup> When the allylation reaction is mediated by indium in water, the reaction proceeds smoothly at room temperature without any promoter.

The reaction of dianions with electrophiles combines two consecutive reactions in a single step, thus resulting in an increase in synthetic efficiency. The generation of dianion equivalents in water was studied through indium mediated bis-allylation of dihalides **1** and dilialides **2** with a variety of carbonyl compounds.<sup>4</sup>

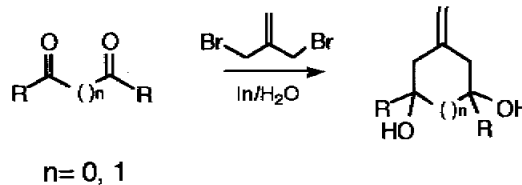


### Indium and Tin Mediated Allylation of 1,3-Dicarbonyl Compounds.

The addition of an organometallic reagent to the carbonyl group of 1,3-dicarbonyl compounds to form a nucleophilic alkylation product is a potentially useful reaction in organic synthesis. However, due to the high acidity of the hydrogen on the carbon alpha to the two carbonyl groups, such an addition has not been widely utilized. A simple, efficient, and general approach to the carbonyl allylation of 1,3-dicarbonyl compounds can be carried out based on the Barbier-type reaction using water as the solvent.<sup>5</sup> Both indium and tin give high yields of the products for this transformation. The use of zinc is less effective. Various 1,3-dicarbonyl compounds were allylated in this way.

### Indium and Zinc Mediated Cyclization Reaction

Cyclopentanoids constitute one of the most common structural features of many natural and synthetic products. Many research efforts have been devoted to their formation.<sup>6</sup> An annulation methodology has been developed based on the indium mediated allylation reaction in water.<sup>7</sup> Various compounds have been transformed to bicyclic, spiral, or simple cyclopentanoids. A related study on the cyclization reaction is the formation of 5 and 6-membered rings via the reaction of 3-bromo-2-bromomethylpropene and a dialdehyde.<sup>8</sup> (Eq. 1).



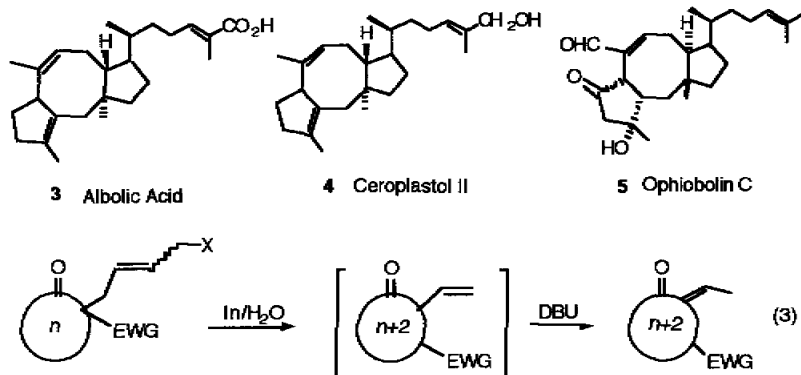
### Metal Mediated Allenylation-Propargylation of Carbonyl Compounds

The metal mediated reaction of propargyl bromide with aldehydes in water can give either the propargylation or the allenylation product. The effects of a variety of metals on the product distribution were examined. The use of

the most reactive metal mediator, indium, also provided the highest selectivity, with a preference for formation of the homopropargyl alcohol. On the other hand, the reaction of an aldehyde with 4-bromo-2-butyne-1-ol gives a mixture of allenylation-propargylation products with a regio-selectivity totally different from that of the non-hydroxylated bromide analogs. The presence of a hydroxyl group on the propargyl bromide moiety was found to strongly affect the selectivity in product formation. Treatment of the aldehyde with *n*-propyl- substituted rather than hydroxyl substituted propargyl bromide underwent allenylation specifically.

### Metal Mediated Two-Atom Carbocycle Enlargement in Aqueous Medium

The importance of medium size (8, 9, 10) rings in organic chemistry is exemplified by their presence as the structural core of a large number of biologically important natural products. In conjunction with our efforts at synthesizing medium ring-based natural products, e.g. alibolic acid (**3**), ceroplastol II (**4**), and ophiobolin C (**5**), five-, six-, seven-, eight-, nine-, ten-, and fourteen-membered rings were enlarged by two carbon atoms into seven-, eight-, nine-, ten-, and fourteen-membered ring derivatives, respectively (Eq. 2) through indium or zinc mediated ring expansion reactions. The use of water as a solvent was found to be critical for the success of the reaction.



### Ruthenium Catalyzed Isomerization of Olefinic Alcohols

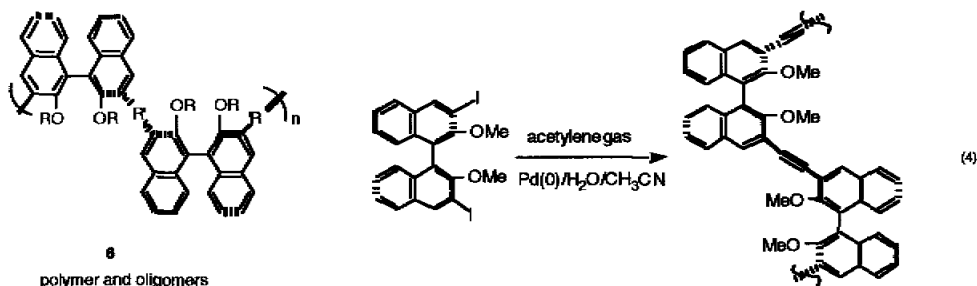
Repositioning the functionalities of olefinic alcohols is a common process encountered in synthesis. Such transformations often require multi-step reactions or strong acids.<sup>9</sup> It was found that in the presence of a catalytic amount of  $\text{RuCl}_2(\text{PPh}_3)_3$ , homoallylic alcohols and allylic alcohols undergo structural reorganization in which both the hydroxyl group and the olefin are reshuffled.<sup>10</sup> The reaction can be conceived of as an olefin migration followed by an allylic rearrangement. Allyl alcohols are rearranged similarly. The use of water is critical to the success of this reaction.

Under the catalysis of  $\text{RuCl}_2(\text{PPh}_3)_3$ , a variety of diols react with homoallylic alcohols, generating mono-allyl ethers. Di-, tri-, and tetra-(ethylene glycol) all react to give mono ethers.<sup>11</sup> Under the same conditions, primary hydroxyls react preferentially over secondary hydroxyl groups.

### Organic Material Synthesis in Aqueous Medium

A particular interest from this laboratory since several years ago has been on binaphthol-based main chain polymers and oligomers (**6**). These binaphthol-based polymers and oligomers were initially proposed for their potential applications as nonlinear-optical materials, electronic conducting materials, chiral ligands for catalysis and host molecules for molecular recognition. The study extends to other poly(areneethynylene)s, an important class of conjugated polymer exhibiting properties such as photoluminescence,<sup>12</sup> electronic conductivity, and nonlinear optics.<sup>13</sup> Previously, Areneethynylene polymers and oligomers have been synthesized by the copolymerization of aryl dihalides with aryl diacetylenes (requiring multistep synthesis) with the use of triethylamine as solvent. We found that the coupling of various aryl iodides with acetylene gas proceeded efficiently in aqueous medium with either water-soluble or insoluble palladium catalysts.<sup>14</sup>

The success of this study resulted in the synthesis of a variety of (p-arene-ethynylene) polymers and oligomers through the aqueous polymerization (Eq. 4).<sup>15</sup> The polymer(oligomer) is similar to the corresponding polymer prepared through the palladium-catalyzed Stille reaction<sup>16</sup>



by a modified procedure of Cummins<sup>17</sup> using bis- (tributylstannyl)acetylene in refluxing 1,4-dioxane.

### Acknowledgments

The research presented herein is attributed to a group of dedicated coworkers whose names appear in the references. We are grateful to many helpful discussions with our colleagues at Tulane. We also thank support of the research by Tulane University, Center of PhotoInduced Process (NSF-LEQSF), DOE-EM and the Petroleum Research Fund (American Chemical Society).

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## OPPORTUNITIES OFFERED BY INDIUM-PROMOTED CARBON-CARBON BOND-FORMING REACTIONS IN WATER

Leo A. Paquette

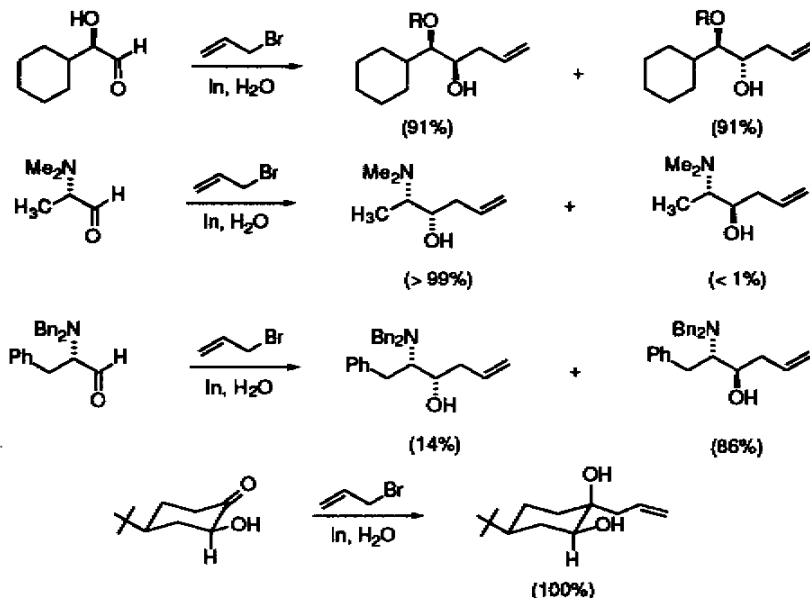
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In line with one of the EPA's long-range goals to reduce risks to the environment posed by existing practices in chemical and pharmaceutical manufacturing, we have been striving to develop the use of organometallic reactions in water in order to prevent pollution at its source. For this thrust to be successful, the processes performed in aqueous solution must be efficient, equivalently useful to or better than their organic-media counterparts, amenable to high stereocontrol as needed, and conducive to generating effluents free of environmental contaminants. In our view, indium is showing great promise as a metal of choice for effecting selected types of carbon-carbon bond-forming reactions in water.<sup>1</sup> Its intrinsic properties lend itself especially well to this particular application. Thus, indium is affected neither by boiling water nor alkali,<sup>2</sup> and does not form oxides when exposed to air.<sup>3</sup> Its first ionization potential (5.785 eV)<sup>4</sup> provides for, but does not demand, operation of electron transfer chemistry.<sup>1a</sup> Also, indium is non-toxic, having found considerable use in dental alloys, and can easily be recovered from its salts by simple electrochemical deposition on the aluminum cathode in a conventional electrolysis unit.<sup>5</sup> Thus, its efficient regeneration in the processes to be described below is guaranteed.

The ability of indium to promote allylations<sup>4-9</sup> and aldol reactions<sup>10</sup> in water as the reaction medium has been amply demonstrated in the recent past. Accordingly, our early studies have been directed toward assessing whether or not diastereoselectivity is capable of being modulated by substitution of the carbonyl substrate at C<sub>α</sub> or

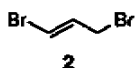
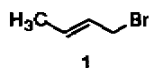
C<sub>β</sub> with suitable heteroatomic functional groups. At issue was whether the phenomena encompassed by the Cram chelate rule and allied considerations would be damped considerably in water, a significantly more polar, hydrogen-bonding medium. All indications now point to the fact that coordination of the substrate to the indium ion very effectively overrides those solvation forces that would break down the chelate, particularly if the neighboring substituent is a free hydroxyl (Scheme 1).<sup>11,12</sup> Under these circumstances, the relative stereochemistry of the newly generated hydroxyl function is introduced syn with respect to that resident on the adjacent stereogenic center. Methoxyl and MOM groups are also acceptable stereodirectors, but more sterically bulky α-oxygenated, α-thia, and most α-nitrogen groups (with the exception of N,N-dimethylamino)<sup>13</sup> are not similarly complexed. In these cases, the couplings are anti-selective, presumably because of adoption of Felkin-Anh transition states in the aqueous environment.

The reported data are especially exciting since they provide convincing evidence that the allylindium reagent holds a very special position in chelation-directed stereocontrol that often substantially exceeds that of other metals. This is so even when the indium-reactions are carried out at 25 °C, well above the temperatures employed under other circumstances. Since unprotected hydroxyl substituents do not lend themselves to anhydrous organometallic reactions, a clear advantage for indium-promoted condensations is apparent since protection-deprotection of sensitive functionality is no longer necessary. Competitive experiments have revealed further that chelation to hydroxyl within the electrophile is accompanied by kinetic acceleration as it should be.<sup>11</sup>



Scheme 1

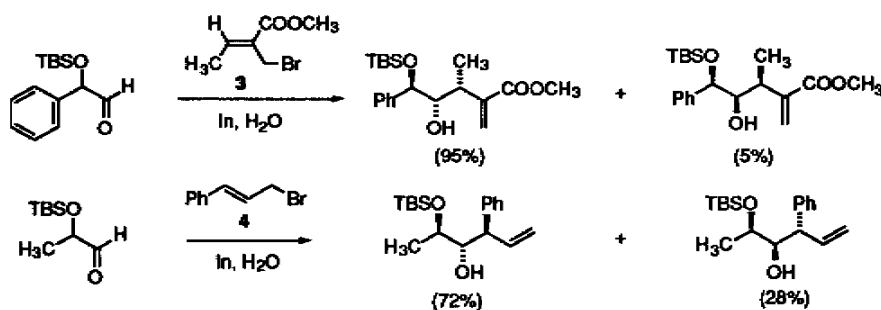
For extended application of the aqueous indium-promoted couplings in synthesis, it becomes highly desirable to be capable of producing alicyclic compounds carrying multiple stereogenic centers in diastereoselective fashion. While the highly utilitarian interdependence of metal and allylic double bond geometry is presently well understood for other metals and has been conveniently classified,<sup>14</sup> only recently has the profile for indium yielded to analysis. Crotyl bromide (**1**) is readily available and has therefore been accorded considerable attention. However, no *x*-facial discrimination is seen when **1** is coupled to benzaldehyde (syn/anti = 50:50).<sup>14,15</sup> When an α-alkoxy<sup>16</sup> or α-acetoxyaldehyde<sup>17</sup> is made the reaction partner, the situation is further exacerbated. No anti,syn product is formed, but the other three diastereomers are produced rather indiscriminately.<sup>16</sup> Although the situation worsens when 1,3-dibromopropene (**2**) is involved in place of **1**,<sup>16</sup> considerable improvement materializes when ethyl 4-bromocrotonate<sup>15</sup> and γ-bromocrotonitrile<sup>18</sup> are utilized. These electronegatively substituted halides furnish product mixtures rich in the anti isomer.



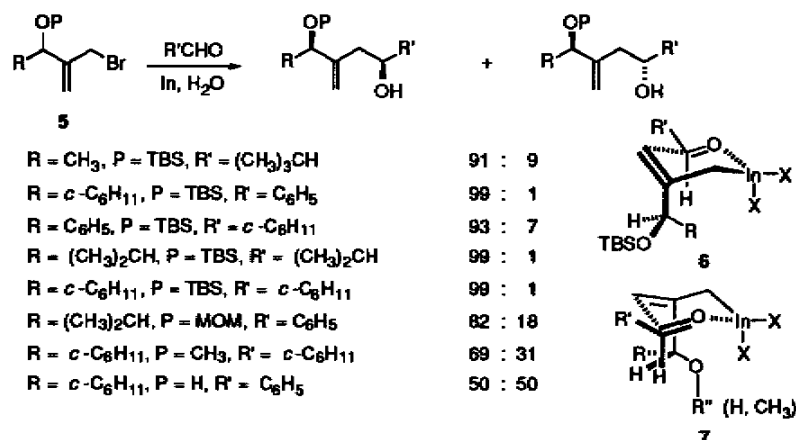
We have attributed the lack of stereocontrol in these circumstances to facile *EIZ* equilibration within the indium reagents derived from **1** and **2**,<sup>16</sup> in a manner compatible to their Grignard, potassium, and lithium derivatives. This important implication has been subjected to experimental test.<sup>19</sup> On the basis of molecular modeling studies and companion experiments, Buchholz and Hoffmann have established that (*Z*)-2-bromomethyl-2-butenolate (**3**) is significantly more thermodynamically stable than its *E* isomer because of the steric bulk of the carbomethoxy group.<sup>20</sup> The energetic disadvantages that would accompany this double bond rotation should carry over directly to organometallic derivatives such as that based on indium. Similar considerations apply to cinnamyl bromide (**4**), except that the *E* isomer is favored here.<sup>21</sup> The dichotomy in diastereoselection exhibited by **3** and **4** is exemplified in Scheme 2.

These findings demonstrate that highly functionalized acyclic molecules containing three contiguous stereogenic centers can be assembled with high stereoselectivity from simple building blocks in water as the reaction medium. Provided that the geometry inherent in the allylindium reagent is highly biased in either an *E* or *Z* sense, control of product stereochemistry can be expected to operate at synthetically practical levels in predictable directions.

Scheme 2



The capacity of indium-promoted reactions for attempting useful levels of long-range asymmetric induction in water as the reaction solvent is likewise remarkable. In related studies carried out independently by the Mulzer<sup>22</sup> and Paquette groups,<sup>23</sup> allylic bromides such as **5** having different coordination potential and steric demands have been reacted with the objective of identifying the relative importance of polar, steric, and chelation factors during 1,4-asymmetric induction. High syn stereoselectivity (91-99%) has invariably been observed when the oxygen in **5** carries a large *tert*-butyldimethylsilyl substituent. Interestingly, this level of stereocontrol is eroded and reactions proceed more rapidly when the steric bulk of the O-protecting group is reduced to the methoxy and hydroxy levels. These findings are consistent with the intervention of transition state **6** in the first instance. The controlling factor appears to be the overall size of the OTBS substituent. The dropoff in  $\pi$ -facial differentiation with *kinetic acceleration* is interpreted to reflect the operation of chelation effects during oxidative addition of



indium into **5** when P = H or CH<sub>3</sub>, but not during the coupling stage. Presumably, the entrance of an aldehyde into the coordination sphere of the indium disrupts internal chelation to the proximal oxygen giving rise to **7** and competitive formation of the and diastereomer.

In Scheme 1, the fastest reactions involving chelation of the allylindium reagent to the  $\alpha$ -hydroxyl substituent were the most stereoselective. By comparison, the slowest reactions in Scheme 3 deliver the highest levels of asymmetric induction. Whether the same sensitive dependencies will operate in other contexts remains to be elucidated.

### Acknowledgment

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### LIPASE-CATALYZED RING-OPENING POLYMERIZATIONS

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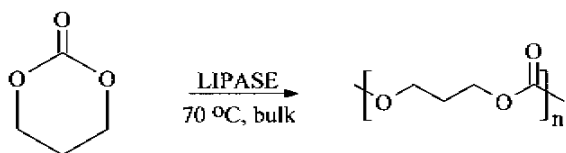
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Trimethylene carbonate  
(TMC)

Poly(TMC)

#### ABSTRACT

This work was directed at extending the use of lipase-catalyzed ring-opening polymerizations to cyclic carbonate monomers.

#### Scheme 1

In addition, a review of background literature of related work is presented.

### INTRODUCTION

The use of enzyme-catalysis in organic media for polymer forming reactions is gaining increasing attention. The hallmark of enzymes is their ability to achieve high enantio- and regioselectivity for various chemical transformations.<sup>1</sup> Furthermore, enzymes represent a family of 'environmentally friendly' catalysts. Advantages of using enzymes in organic as opposed to aqueous media are as follows: *i*) increased enzyme thermal stability, *ii*) solubility of a wide range of substrate types in the reaction media, *iii*) no requirement for pH adjustment as the reaction proceeds and *iv*) enzymes are readily recyclable.<sup>2,3</sup> The application of these reactions to lipase-catalyzed lactone ring-opening polymerizations are described below.

Studies of enzyme-catalyzed lactone ring-opening polymerizations in organic media have been conducted for the polymerizations of  $\epsilon$ -caprolactone ( $\epsilon$ -CL),<sup>4,6</sup>  $\delta$ -valerolactone ( $\delta$ -VL),<sup>4</sup>  $\beta$ -propiolactone,<sup>7</sup> ( $\pm$ )- $\beta$ -methyl- $\beta$ -propiolactone,<sup>7</sup> ( $\pm$ )- $\alpha$ -methyl- $\beta$ -propiolactone<sup>8</sup> and  $\gamma$ -butyrolactone.<sup>7</sup> The enzyme-catalyzed co-polymerization of  $\beta$ -propiolactone with  $\epsilon$ -CL was also investigated.<sup>9</sup> Enantioenriched polymers were obtained by the



stereoselective enzyme-catalyzed polymerization of ( $\pm$ )- $\alpha$ -methyl- $\beta$ -propiolactone.<sup>9</sup> Mechanistic investigations into lipase catalyzed reactions are further exploiting enzymes as catalysts. For example, porcine pancreatic lipase (PPL) catalyzed  $\epsilon$ -CL polymerizations were shown to provide "controlled" polymerizations where the molecular weight was a function of the reaction monomer to initiator stoichiometry.<sup>10</sup> In general, polymerizations of 4- to 7-membered ring lactones resulted in low molecular weight products after long reaction times. Additional mechanistic studies will be needed to improve propagation kinetics and product molecular weights.

In contrast to the studies described above with small ring-size lactone monomers, enzyme-catalyzed polymerizations of macrolactones have already resulted in improved propagation kinetics and/or molecular weights when compared to chemical preparative routes. The enzyme-catalyzed polymerization of  $\omega$ -undecanolide (UDL),  $\omega$ -dodecanolide (DDL) and  $\omega$ -pentadecanolide (PDL) (12-, 13- and 16-membered lactones) were first investigated by Kobayashi and co-workers.<sup>11-13</sup> Recently, we reported the ring-opening polymerization of  $\omega$ -pentadecalactone (PDL) catalyzed by immobilized and non-immobilized forms of the lipase PS-30.<sup>14</sup> When immobilized PS-30 was used for bulk polymerizations at 70 °C we obtained poly(PDL) with a high number average molecular weight ( $M_n$  = 62,000 g/mol) and moderate dispersity ( $M_w/M_n$  = 1.9).<sup>14</sup> Further study of this enzyme-monomer system showed that reaction water content and temperature were important factors that controlled not only the rate of monomer conversion, but also the polymer molecular weight.<sup>14</sup> Specifically, we showed that by decreasing the water content in reactions, slower polymerization rates but higher poly(PDL) molecular weights resulted. Furthermore, poly(PDL) molecular weights were highest at reaction temperatures between 80 and 90 °C. One objective of this paper was to determine how the above reaction parameters would effect lipase-catalyzed ring-opening polymerizations carried out with a different enzyme-monomer pair.

A number of aliphatic polycarbonates and their copolymers were reported to be environmentally biodegradable and are of interest as bioresorbable biomedical materials.<sup>15,16</sup> Also, cyclic carbonates have been recognized as a novel class of monomers showing expansion in volume on polymerization.<sup>17</sup> Ring-opening polymerization of 1,3-dioxan-2-one (TMC) was first studied by Carothers and Van-natta.<sup>18</sup> More recent investigations have reported the polymerization of TMC to linear high molecular weight chains by using organometallic catalysts.<sup>19,20</sup> Early work by Abramowicz and Keese<sup>21</sup> reported the enzymatic transesterification of diphenyl carbonate, DPC, with a wide variety of alcohols and phenols. The reaction products included the substitution of one or both of the phenoxide groups on DPC. Transesterification of DPC with bifunctional alcohols catalyzed by the *Candida* lipase resulted in the synthesis of oligocarbonates having molecular weights of about 900 g/mol.<sup>21</sup> Based on the work of Abramowicz and Keese,<sup>21</sup> a preliminary report of lipase-catalyzed carbonate polymerization by us<sup>22</sup> and other studies described above using lactones, it appeared possible that cyclic carbonate enzyme-catalyzed polymerization might provide a route to linear polymers of substantial molecular weight. Furthermore, within a similar time period as our report<sup>22</sup>, Matsumura *et al*<sup>23</sup> and Kobayashi *et al*<sup>24</sup> also communicated results on the lipase-catalyzed polymerization of TMC. Matsumura *et al*<sup>23</sup> claimed that extraordinarily high molecular weight poly(TMC) ( $M_w$  = 156,000 g/mol,  $M_w/M_n$  = 3.8) was obtained by using only low quantities of PPL (~0.1 wt %) as the catalyst at very high reaction temperature (100 °C).<sup>23</sup> In contrast, Kobayashi *et al*.<sup>24</sup> reported the formation of low molecular weight poly(TMC) ( $M_n$  = 800 g/mol,  $M_w/M_n$  = 1.4) by PPL (50.0 wt %) catalyzed polymerization at 75 °C. Indeed, comparison of the communications in references 22, 23 and 24 showed considerable points of variation which, in part, was further explored in this work.

In this paper, we summarize the results of a study on the effects of reaction parameters on the lipase-catalyzed ring-opening polymerization of cyclic carbonates.

## RESULTS

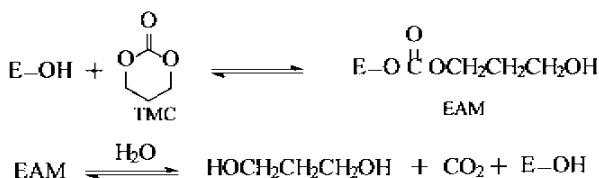
Of the seven lipases screened for bulk trimethylene carbonate (TMC) polymerization (70 °C, 120 h), Novozym-435 from *Candida antarctica* gave almost quantitative monomer conversion (97 %), and poly(TMC) with an  $M_n$  = 15,000 g/mol ( $M_w/M_n$  = 2.2) with no apparent decarboxylation during propagation. The lipases from *Pseudomonas* (AK and PS-30) and *Mucor* (MAP-10) species also exhibited high monomer conversions (>80%, 120 h) but gave lower molecular weight polymers with broad polydispersity. Analyses by <sup>1</sup>H-NMR spectroscopy suggested that poly(TMC) prepared by Novozym-435 catalyzed polymerization had terminal -CH<sub>2</sub>-OH functionalities at both chain ends. A monotonic increase in monomer conversion with time and the rapid increase in  $M_n$  as a function of monomer conversion for Novozym-435 catalyzed TMC bulk polymerization at 70 °C suggests that the polymerization has chain-type propagation kinetics. Increase in conversion above 66 % did not substantially change  $M_n$ . The %-conversion was larger when the reaction temperature was increased from 45 to 55 °C. Further increase in the reaction temperature from 55 to 85 °C did not give higher %-conversion values. The molecular weight decreased substantially as the reaction temperature was increased from 55 to 85 °C ( $M_n$  from

24,400 to 5,900 g/mol). The highest poly(TMC) molecular weight ( $M_w \sim 24,400$  g/mol) was obtained by conducting the polymerization at 55 °C. Monomer conversion and molecular weight as a function of the %-reaction water content (w/w) was investigated. Increasing the water content resulted in enhanced polymerization rates and decreased molecular weights. Separation of the oligomeric products from polymerizations of TMC in dried dioxane and toluene catalyzed by porcine pancreatic lipase led to the isolation of di- and triadducts of trimethylene carbonate. Based on the symmetrical structure of these products and the end-group structure of high molecular weight chains, the following mechanism for chain initiation and propagation for lipase-catalyzed TMC polymerization was proposed.

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### Initiation:

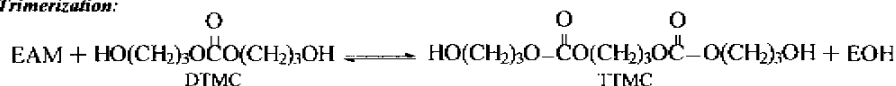


### Propagation:

#### Dimerization:



#### Trimerization:



#### Polymerization:



Scheme 2

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# **SOLVENTLESS/SOLID STATE PROCESS**



## SOLVENTLESS ORGANIC REACTIONS USING MICROWAVES

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### ABSTRACT

A solvent conserving strategy for organic transformations is described that uses neat reactants in solventless systems. The reactions are assisted by benign catalysts or the surfaces of recyclable solid support(s) such as alumina, silica and clay. These rapid processes are facilitated by microwave activation and enable the effective utilization of several supported reagents, namely, iodobenzene diacetate-alumina, periodate-silica and iron(III) nitrate-clay etc. under solvent-free conditions. The environmentally benign aspects of this approach is discussed for synthetically useful deprotection, condensation, cyclization, oxidation and reduction reactions that encompass industrially important compounds and intermediates such as enones, enamines, nitroalkenes, oxidized sulfur species and heterocycles.

### INTRODUCTION

*"Preventing pollution and minimizing waste generation gradually will replace cleaning up **sins of the past**".*<sup>1</sup> This shift in paradigm dictated, in part, by landfill shortages and increased public awareness is noticed by the public as well as environmental industry.<sup>1</sup> Eventually, the focus is shifting from cleaning up old environmental problems to reducing or preventing the new ones wherein pollution prevention 'at source' is replacing end-of-the-pipe control technology. In the environmentally conscious era, the role of chemistry and chemists involved is to incorporate processes and design products which can eliminate or minimize the generation of associated pollutants. Consequently, the ideal approach may comprise **source reduction, recycling and lastly the treatment of waste**, in that order of preference. Importantly, the younger generation of responsible chemists should be introduced to this change in thinking so that these novel concepts can be incorporated in the planning, development, and expansion stages of the projects that are friendlier to the environment thus evolving *green* chemistry.

### THE APPROACH

The salient feature of the chemical conserving technology is that common synthetic reactions are performed using microwave (MW) activation either in the presence of a catalyst or catalyzed by the surfaces of recyclable solid support(s) under solvent-free 'dry' conditions. Thus, the problems associated with waste disposal of solvents (used several fold in chemical reactions) and/or excess chemicals are avoided or minimized culminating in waste reduction and the prevention of chemical pollution 'at source'. These environmentally benign protocols are of wider application to synthesis of a wide variety of industrially important compounds and intermediates namely, enones, imines, enamines, nitroalkenes, oxidized sulfur species and heterocycles which, when otherwise obtained by conventional procedures contribute to the burden of chemical pollution.

### THE RATIONALE

Capitalizing on our observation that alumina-mediated solvent-free cleavage of esters takes place (presumably catalyzed by exposed aluminum ions and hydroxide groups on surface) in the absence of added reagents,<sup>2</sup> we have achieved a tremendous enhancement of this reaction upon exposure to microwaves. MW irradiation has been used for several applications including organic synthesis in a variety of solvents.<sup>3-6</sup> The reactions conducted using MW involve absorption of microwave energy by polar molecules, non-polar molecules being inert to microwave dielectric loss. However, in these solution-phase reactions,<sup>4,6</sup> the development of high pressures and use of specialized Teflon vessels are some of the major limitations.

A practical dimension to the microwave heating protocols has now been added by conducting reactions under 'dry' conditions<sup>7-19</sup> wherein the organic compounds adsorbed on the surface of inorganic oxides, such as alumina, silica gel and clay, absorb the microwaves whereas the solid support does not absorb nor restrict their transmission. This solvent conservation has an enormous impact on reduction of waste discharge since *solvents are often used in quantities 50-100 times those of the reacting materials*.

### ENVIRONMENTAL BENEFITS OF THE TECHNOLOGY

- i) **No solvents or toxic chemicals** (e.g. acids, bases or salts) are required and even mixing is not necessary—microwaves are neither absorbed nor their transmission restricted by mineral supports like

silica, alumina, clay, or supported reagents.

- ii) **No additional steps** in manipulations are often needed—the reaction products are normally adsorbed on the chromatographic materials for usual purification purposes.
- iii) **Few wasteful byproducts** are generated—the solid supports and catalysts ('doped' supports) are **recyclable**.
- iv) **Improved synthetic procedures** are evolved—generation of pure products (specificity) in good yields as a consequence of enhancement of reaction rates.

## SUMMARY OF RESULTS

The success and practical feasibility of the strategy, that is applicable to the synthesis of industrially important compounds, has been demonstrated<sup>7-17</sup> by MW cleavage reactions,<sup>7-11</sup> deprotection of protected alcohols, phenol, and carbonyl compounds on solid supports,<sup>11</sup> dehydration reactions leading to the synthesis of alkenes, enones, imines, enamines,<sup>12-13</sup> nitroalkenes,<sup>14</sup> solid state oxidation,<sup>15</sup> reduction<sup>16</sup> and expeditious one-pot preparation of heterocycles using benign catalysts.<sup>17</sup>

The general procedure involves simple mixing of the reactants with the catalyst, in liquid or solid state, or their adsorption on solid supports (neat or in minimum amount of solvent for adsorption).

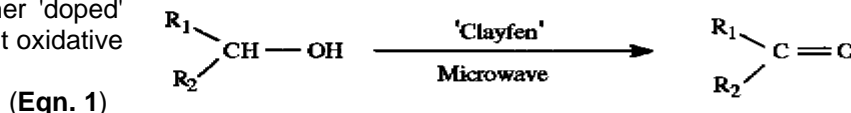
## CLEAVAGE REACTIONS-DEPROTECTION OF PROTECTED GROUPS

Protection and deprotection sequences find routine applications in the synthesis of monomer building blocks, fine chemicals and pharmaceutical intermediates and are, often, carried out using acidic, basic or sometimes toxic and corrosive reagents. We have successfully demonstrated the use of MW for rapid deprotection of protected aldehydes,<sup>8,11</sup> alcohols,<sup>7</sup> including desilylation<sup>9</sup> and debenzylolation reactions.<sup>10</sup>

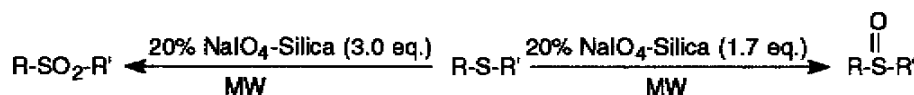
The solvent-free debenzylation approach may find application in facile peptide bond formation that would eliminate the use of *irritating and corrosive chemicals such as trifluoroacetic acid and piperidine*.

## OXIDATION OF ALCOHOLS, SULFIDES AND THIOPHENES

The routinely used oxidizing reagents for organic functionalities are peracids, peroxides, potassium permanganate (KMnO<sub>4</sub>), chromium trioxide (CrO<sub>3</sub>), potassium chromate (K<sub>2</sub>CrO<sub>4</sub>), and potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>). Using Clayfen in solid state and in amounts that are half that of used in earlier studies, a rapid synthesis (15-45 sec) of carbonyl compounds in high yields is achieved (Eqn. 1).<sup>15</sup> Other 'doped' surfaces are being optimized for efficient oxidative protocols.



The generation of sulfoxides, important building blocks for a number of useful chemicals, needs strenuous procedures and toxic chemical reagents like hydrogen peroxide, nitric-, chromic acid and peracids. Oxidation to sulfones requires ruthenium trichloride, HOF-CH<sub>3</sub>CN, and chromium trioxide-acetic acid. Using microwaves the desirable selectivity has been achieved in oxidation of sulfides to sulfoxides and sulfones (Eqn. 2) by using periodate 'doped' silica gel and reaction time (pulsed techniques).



periodate 'doped' silica gel and reaction time (pulsed techniques).

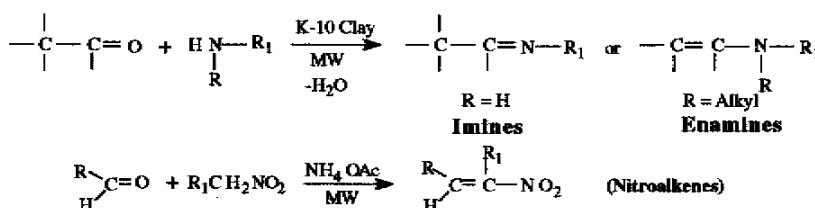
(Eqn. 2)

## SYNTHESIS OF IMINES, ENAMINES, NITROALKENES AND HETEROCYCLES

The driving force for these reactions is the elimination of a water molecule which is often brought about by azeotropic distillation in the presence of *p*-toluenesulphonic acid, molecular sieves and titanium chloride.

MW-assisted dehydration by catalytic montmorillonite K-10 clay<sup>12</sup> or supported reagents<sup>13</sup> such as Envirocats® in the reactions of amines with aldehydes and ketones, respectively, under solventless conditions results in a facile preparation of imines and enamines (Scheme-1).

(Scheme-1)



The Henry reaction, condensation of carbonyl compounds with nitroalkanes to afford nitroalkenes, proceeds rapidly *via* this MW approach in presence of catalytic amounts of ammonium acetate in the neat reactants thus avoiding the use of a large excess of polluting nitrohydrocarbons solvents normally employed (**Scheme-1**).<sup>14</sup>  $\alpha,\beta$ -unsaturated nitroalkenes provide easy access to a vast array of valuable building blocks and precursors for a range of intermediates useful to pharmaceutical and chemical industry that include nitroalkanes, N-substituted hydroxylamines, amines, ketones, oximes, and  $\alpha$ -substituted oximes and ketones.<sup>22</sup> A convergent one-pot synthesis of bioactive benzopyrans<sup>23</sup> has been achieved by generating the nitrostyrene/enamine derivatives *in situ* and inducing subsequent reactions with o-hydroxyaldehydes.<sup>17b</sup> The cyclization of 2'-aminochalcones on clay provide an easy access to 2-aryl-1,2,3,4-tetrahydro-4-quinolones, valuable precursors for medicinally important quinolones.<sup>17a</sup>

This technology, that can be scaled up in either a batch or continuous process,<sup>24</sup> addresses the needs of broad chemical community base that includes *pharmaceutical, polymer, and fine chemical areas*. Besides *pollution preventive*, these processes are superior to the existing ones in terms of *time, ease of manipulation and selectivity*.

### DESTRUCTION OF HAZARDOUS WASTES-REGENERATION OF SUPPORTS

The "ripple effect" from this technology is extendible to the degradation of toxic materials present in the soil or adsorbed pollutants on solid supports (charcoal). In view of the existing emission problems associated with the high temperature incineration reactions, localized heating by MW in presence of suitable catalysts provides a viable solution for the safe removal or disintegration of compounds bearing nitro-, halo-, or thiosubstituents from the contaminated soils, water or air; MW activation has promise for successful destruction or elimination of nitro- and chloroarenes under solvent-free conditions in presence of iron salts and hydrogen donors.<sup>21</sup>

### ACKNOWLEDGMENTS

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## POLLUTION-PREVENTING LITHOGRAPHIC INKS

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### ABSTRACT

A pollution-preventing lithographic ink system works conventionally at a pH less than 7, but becomes its own emulsifying agent at high pH. Accordingly, it can be washed off lithographic printing presses with aqueous base. The emulsification kinetics of the ink have been experimentally studied as mass transfer coefficients under the conditions of low shear. Correlations for this mass transfer suggest that washing is controlled by diffusion of components within the ink. The results point toward a strategy for achieving other pollution-preventing technologies.

### INTRODUCTION

Printing often causes pollution. Much of this pollution comes from the ink, especially from cleaning the ink from the presses. The ink itself can contain an aliphatic solvent; the cleaning usually involves aliphatic and aromatic solvent blends. The evaporation of these solvents and their discharge in waste streams is significant. For example, a typical medium size coldset web plant uses 40,000 kg per year of ink, of which 6,000 kg is lost as emissions. The plant uses over 10,000 kg per year of cleaning solutions, all of which is lost. A typical newspaper uses over 100,000 kg per year of ink and emits over 8,000 kg of volatile solvents (Pennaz, 1994a).

A recently announced ink avoids pollution by these volatile solvents (Pennaz, 1994b; Pennaz and Schacht, 1994). The new ink does not contain aliphatic solvents, so that its use produces virtually no emissions during printing. Moreover, this ink becomes a good emulsifying agent under basic conditions. As a result, the printing itself involves no solvent, and the cleaning of the presses is effected by washing with water at slightly elevated pH. Thus the new ink completely avoids the solvent emissions commonly associated with printing.

This paper explores the kinetics of this new ink. The main components of an ink are an oil, a resin, and a spectrum of other species including pigments. The oil and resin are the most important components. The oil is a natural product containing triglycerides of fatty acids with unsaturated double bonds. Linolenic, linoleic and oleic acids are examples. These triglycerides react with oxygen in the air to crosslink, making the ink permanent. The alkyd resin is a nonvolatile, synthetic, low molecular weight polyester with pendant aliphatic and carboxylic acid groups, similar to resins made for use in paints. In its acid form, it is hydrophobic, but as a sodium salt, it is sufficiently hydrophilic to act as an emulsifier. Thus during printing, the resin is hydrophobic; but during clean-up, it becomes emulsifiable in an aqueous solution at an increased pH.

The keys to the new ink's value are not only its strong performance in printing, but also its kinetics during clean-up. We have studied these kinetics by measuring the rate of neutralization of the wash solution, organizing our measurements as mass transfer coefficients. Our results are summarized below.

### RESULTS

The most important results are shown in Figure 1. These results show that the mass transfer coefficient times the area per volume  $ka$  is proportional to the stirring rate times the resin concentration, divided by the product of the hydroxide concentration and the viscosity. This variation can be predicted by assuming that hydroxide is the limiting reagent, and that the reaction between hydroxide and resin occurs at a solid-solid interface between reacted soap and unreacted resin (Bhaskarwar and Cussler, 1997). The soap accumulates and then is removed by shear. Other mechanisms, including those ordinarily cited for conventional emulsification, are not consistent with the experimental results.

More generally, the issue in this paper is the modification of any product to reduce its environmental impact. In the case of the ink, the ink's cleanup is facilitated without in any way compromising the quality of the ink's printing. Generalizing this issue is most straightforward for other forms of lithography, like those used in manufacture of microelectronic devices. Similar generalizations might be found for solvent-based paints and varnishes, especially coatings used to treat raw wood where water-based latex can disrupt the grain. These generalizations may work because the resin chemistry used for the ink studied here is actually borrowed from the paint industry.



In general, new inks or paints or other environmentally-friendly products need not depend on changes in pH. Such changes are one reliable way to alter dramatically the key physical properties. The resin's acid form is highly hydrophobic; its basic form is the emulsifying soap. However, use of acid and base can be corrosive, even dangerous; it will produce a waste stream of salt. Other, still gentler products might use temperature changes. Such changes, in for example ethylene oxide linkages, can produce phase changes, including those due to lower consolute points. Because these changes are not dependent on corrosive chemicals and produce no waste, they would be a more benign extension of the pollution preventing lithography described in this paper.

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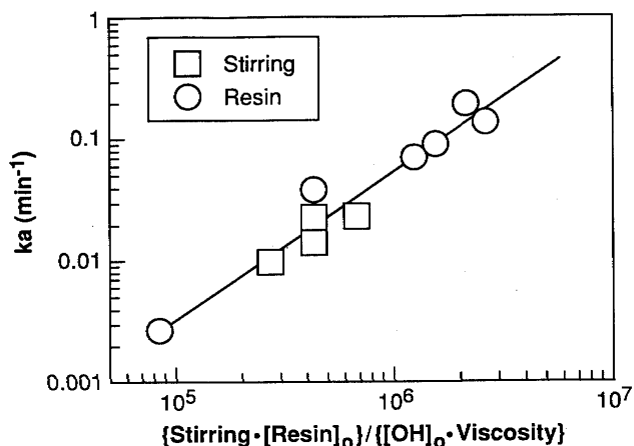


Figure 1. Rate Constant  $k_a$  vs. Process Variables

## VOLATILE METHYL SILOXANES: ENVIRONMENTALLY SOUND SOLVENT SYSTEMS

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### ABSTRACT

Linear volatile methyl siloxanes (VMS) are a class of mild solvents which have an unusual combination of environmentally benign qualities... They are low in toxicity, almost odorless, make almost no contribution to global warming, do not contribute to urban ozone pollution, and do not attack the stratospheric ozone layer. They do not accumulate in the atmosphere, but rather are rapidly transformed to naturally found species. They have received SNAP approval and VOC exemption from the EPA and are not regulated under NESHAP. Their solvency can be tailored to specific applications by use of cosolvents and surfactants. The underlying phenomena to their use to remove particulates, oils, fluxes, and aqueous contaminants will be presented. Many of their applications require the use of highly purified grades which leave no surface residue. Their value in precision Water Displacement Drying (WDD) will be discussed from the perspective of the many processing steps of Flat Panel Display manufacturing.

### INTRODUCTION

The linear volatile methyl siloxanes are low molecular species which contain only silicon, carbon, hydrogen, and oxygen. Highly purified grades are commercially available of the linear dimer, trimer and tetramer as Dow Corning® OS-10, OS-20, and OS-30 Fluids. These are the permethylated hexamethyldisiloxane, octamethyltrisiloxane, and decamethyltetrasiloxane, respectively.

The low molecular weight and high degree of purity of *Dow Corning* OS Fluids insures that they are totally volatile and leave no silicone residue.

They have an outstanding profile of environmental and toxicological properties.

The mildness of these solvents confers compatibility with a wide variety of plastics and some rubbers. Their solvent strength is weaker than that of saturated hydrocarbons but stronger than that of the commercially available saturated hydrofluorocarbons. Their solvency may be moderately enhanced by adding moderate amounts of stronger solvents since they are miscible with many such. The addition of very small amounts of

soluble surfactants confers the ability to displace water from aqueous-cleaned parts while retaining their favorable environmental profile.

## HEALTH AND ENVIRONMENTAL PROFILE

Toxicological profile. *Dow Corning* OS-10, OS-20, and OS-30 Fluids are low in toxicity as demonstrated in acute oral, inhalation, and dermal exposure testing; subchronic oral and inhalation studies; and tissue culture biocompatibility and genotoxicity evaluations.

In the acute studies, no adverse effects were observed, even at the maximum achievable doses in laboratory animals; however, it was noted that mild, temporary discomfort might result from eye contact. Subchronic oral and inhalation studies revealed no toxicological responses significant to human health. Tissue culture biocompatibility studies conducted to assess the ability of these fluids to damage or destroy cells revealed no effects for any of the materials tested. Further, the fluids were found to be non-genotoxic in short-term tests for DNA damage or mutation.

Threshold Limit Values (TLVs), which are set by the American Conference of Governmental Industrial Hygienists (ACGIH), have not been established for VMS fluids. However, based on a 90-day study, an Industrial Hygiene Guideline (IHG), defined as the maximum average exposure level to which workers may be exposed over an 8-hour work day, was set at 200 ppm for *Dow Corning* OS Fluids.

Additionally, exposure to hexamethyldisiloxane, the major ingredient of *Dow Corning* OS-120 Fluid, was monitored at two typical electronics assembly facilities. The results of these studies demonstrate that the use of *Dow Corning* OS-120 Fluid for manual cleaning from pressure-dispensed containers can be handled safely by operators in terms of longterm inhalation exposure. For the 14 different operators tested, vapor exposures never reached even 10 percent of the 200 ppm guideline. In addition to hexamethyldisiloxane (91 percent), *Dow Corning* OS-120 Fluid contains propylene glycol ether (9 percent). The IHG of propylene glycol ether is 100 ppm.

Environmental profile. In 1994, the U.S. EPA issued a formal ruling on VMS materials, declaring them exempt from federal VOC regulations.<sup>1</sup> This action was taken in response to a petition and supporting data submitted by *Dow Corning* to demonstrate that VMS fluids do not contribute to air quality problems. Individual states have also been petitioned to request that similar action be taken to coincide with the federal government's exemption. As of February 1997, 45 states, including California, had granted exemption to VMS fluids. (See Table 2, VOC Content, for data specific to *Dow Corning* OS Fluids.)

Further, VMS materials are not regulated as "hazardous air pollutants" (HAPs) and are not controlled under NESHAP requirements or the Clean Air Act National Ambient Air Quality Standards. In 1994, VMS materials were included on a list of acceptable precision and electronics cleaning substances under SNAP. In addition, VMS fluids are not regulated under U.S. EPA Title III Air Toxics and are not EPA Criteria Pollutants.

Due to the volatility of VMS fluids, the most likely route for environmental exposure is through evaporation. VMS materials degrade quickly via ongoing natural oxidation and have an atmospheric life span of just 10-30 days.<sup>2,3</sup> Ultimate degradation products include water-dissolved silica, water, and carbon dioxide, all abundant, naturally occurring, benign compounds. Because VMS fluids are effectively oxidized before reaching the stratosphere, they are believed to have no impact on the earth's protective ozone layer and negligible contribution to global warming. A complete discussion of their atmospheric chemistry will soon be published<sup>4</sup>.

## APPLICATIONS

Typical uses are to remove oils, light greases, and fingerprints while cleaning optics, gyroscopes, fiber optic assemblies, plastics, and sensitive metals. The unmodified VMS provide excellent solvency for non-polar oils and viscous fluids, especially for the high molecular weight silicones. The high molecular weight silicones are a class of materials used in many industries: These can otherwise be difficult to remove (or to deposit from carrier fluids).

The use of VMS to remove semi-polar soils or water requires the use of additives. A number of examples of such solvent modification using additives will be shown in the talk, including the use of reflux or of room temperature azeotropes to provide consistent cleaning performance.

Currently, the water removal step at the end of precision aqueous cleaning processes requires high capital and operating costs for the large volumes of ultra-high purity (UHP) water needed for rinsing to a spot-free finish upon drying. This consideration is important for the manufacture of flat panel displays, memory disks, and microelectronics. In these industries, current methods use hot air-assisted evaporation, capillary pull-out drying, spin-rinse drying, and IPA solubilization. Immiscible fluid displacement drying using hexamethyldisiloxane as the base fluid greatly ameliorates the need for UHP water since dissolved solids and colloids are removed simultaneously with the water.

Recent work has shown some remarkable features of WDD when using lighter-than-water displacement fluids such as VMS. The profound effects upon displacement of the interfacial tension and of dynamic changes to the substrate hydro-philicity or -phobicity will be demonstrated. Furthermore, the benign properties of the VMS are brought fully to bear since the amount of enabling surfactant needed is very small.

## SUMMARY

The linear VMS provide environmentally benign base fluids for precision cleaning and drying of fabricated articles. Their use for precision cleaning requires highly purified grades that are completely volatile. Their solvency may be tailored with additives to broaden their uses to removal or deposition of semipolar oils and viscous fluids as well as to the removal of water by displacement. Their outstanding environmental and toxicological profiles help to ensure that they will be reliably available in industry's repertoire of cleaning and carrier fluids for a long time to come.

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# **ENVIRONMENTAL BENIGN CATALYSIS**



## POLYMER-FACILITATED BIPHASIC CATALYSIS

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### INTRODUCTION

Recently, there has been increased interest in the development of new strategies to use and recover homogeneous catalysts. This interest is a consequence of the interest in improving the efficiency of industrial chemical processes to minimize waste. Here I discuss ways polymers facilitate catalyst separation and reuse in biphasic processes.

The historic role of polymer supports in catalysis is as devices for catalyst separation and reuse. In heterogeneous catalysis, a soluble substrate or product is easily separated from catalyst and the catalyst can typically be reused with little effort. The situation in homogeneous catalysis is different. In homogeneous catalysis, one usually forgoes the advantages of phase separation in catalyst recovery and product purification for the sake of higher or more controllable catalyst activity and selectivity. Ligand-catalyst solubility in homogeneous catalysis generally precludes simple liquid/solid or liquid/liquid phase separation. Catalyst/product separations in homogeneous catalysis is thus often accomplished by processes like distillation if the catalyst solution is to be simply recovered and reused. In other cases, product/catalyst separation requires more complicated steps and catalyst/ligand recovery may not lead to a recoverable reusable catalyst. Most conventional homogeneous catalysts operate in organic solvents and this can lead to a chemical waste problem, especially when post-reaction processing for catalyst/ligand recovery is required. One way to address this issue is to carry out homogeneous catalysis in other solvent systems - notably in water or in supercritical CO<sub>2</sub> media. These other solvent media have attracted recent attention since chemistry that employ these solvents is considered environmentally "friendlier". Separation of catalysts and products in these latter cases presumably would produce less organic solvent waste.

### RESULTS AND DISCUSSION

Polymer-supported ligands were originally introduced as a way to make homogeneous catalysts separable without changing their reactivity.<sup>1-3</sup> This typically involves use of an insoluble crosslinked polymeric ligand to bind the catalyst. However, while crosslinked polystyrene systems remain a conceptually simple and elegant way to solve the problem of homogeneous catalyst/product separation, problems with catalyst leaching, catalyst or ligand characterization, reactivity and catalyst stability have led us to look at other polymer systems.<sup>4</sup>

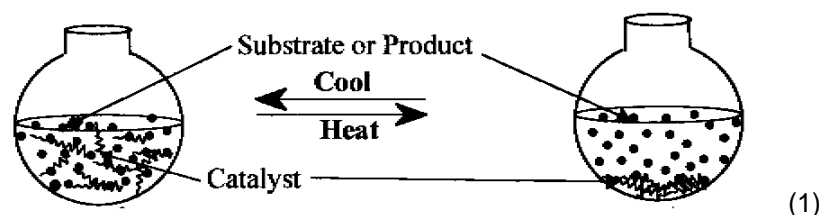
Our first efforts in this regard involved the use of organic phase soluble polymers and our initial studies focused on polyethylene as the polymer support. Two features of polyethylene were of interest in its potential application in catalysis chemistry. First, polyethylene is inert chemically. Thus, this polymer was unlikely to chemically interfere with a bound catalyst. Second and more importantly, polyethylene is a polymer whose solubility is profoundly affected by temperature. Specifically, polyethylene is completely insoluble in all solvents at room temperature but is quite soluble in a number of solvents at higher temperature. We reasoned that this sort of solubility change could be used effectively in catalysis if ligands and thus catalysts could easily be attached to polyethylene. Our expectation was that a polyethylene-bound catalyst would be insoluble at room temperature (and recoverable) but soluble (and active) at high temperature.

The strategy we developed using polyethylene oligomers as ligands to separate, recover and reuse a homogenous catalyst has successfully been used for a number of different catalysts.<sup>4,5</sup> Catalyst recovery is generally quantitative. Catalyst activity mirrors that of a low molecular weight analog so long as the polymer is soluble. However, this strategy has limitations. It requires nonpolar organic solvents — toluene, dichlorobenzene and dibutyl ether. It requires elevated temperatures for ligand or catalyst dissolution and for the steps involved in synthesis of the ligand.

This polyethylene oligomer support work emphasized the utility of separating a polymeric catalysts from solvent and products by cooling, precipitation and filtering. In essence this work relied on what might be termed normal solubility. However, we were aware that many water soluble synthetic polymers precipitate or phase separate from water on heating.<sup>6,7</sup> This phenomenon is also common for other synthetic polymers including nonpolar polymers in non polar solvents although it is often only seen above the boiling point of the solvent.<sup>8</sup> We now have used this phenomena to both prepare "smart" catalysts and to effect catalyst/product/substrate separation

and catalyst recovery.

It is feasible to prepare "smart" catalysts from polymeric ligands that precipitate or phase separate on heating. In these cases, the reactivity of the catalyst is controlled through the temperature dependent phase separation of the polymeric ligand (eq. 1). At low temperatures, the catalyst is soluble and active because the polymer is in solution. At elevated temperatures, the polymer and the attached catalyst phase separates and the catalyst activity decreases. We demonstrated this first with a commercially available ethylene oxide - propylene oxide - ethylene oxide triblock copolymer.<sup>9</sup> Our subsequent work has emphasized poly(*N*-isopropylacrylamide) (PNIPAM) copolymers that separate as water-swollen solid gels on heating.<sup>10</sup>

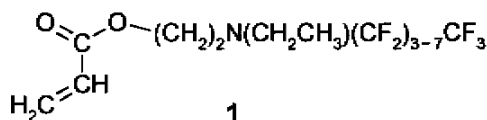


Homogeneous active solution of catalyst, product and substrate at 33 °C

Heterogeneous inactive mixture of catalyst, substrate and product at 39 °C

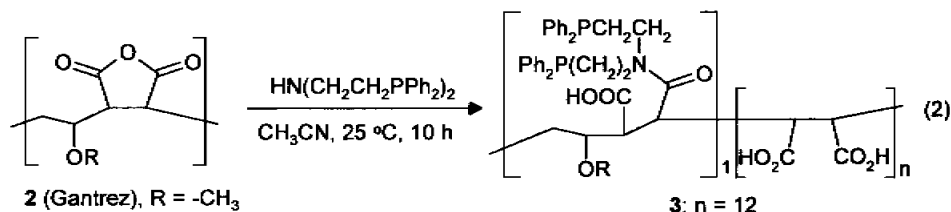
The examples above where soluble polymers effect phase separation of a catalyst have a common theme. Precipitation on cooling of the crystalline polyethylene, precipitation with a poor solvent (PEO or PNIPAM) and precipitation on heating (PNIPAM) all use a polymer to dictate the solubility of a substituent. This engineers solubility and separability into a catalyst by using the solubility and separability of the polymer support without significantly affecting the catalyst's activity. Two recent examples of fluororous phase polymer supports and of amphoteric polymer supports further illustrate this idea.

Fluororous biphasic chemistry is an attractive idea.<sup>11,12</sup> It is a non-aqueous version of aqueous biphasic chemistry. The general idea requires fluororous phase soluble ligands or catalysts to be effective. We have now prepared fluororous phase soluble polymers to which we can attach catalyst ligands.<sup>13</sup> For example, copolymers derived from *N*-acryloxysuccinimide and a fluoroacrylates like **1** react with an aminophosphine ligand to form fluororous phase soluble phosphines that ligate homogeneous catalysts.<sup>14</sup> These polymers are generally useful fluororous phase soluble supports that engender fluororous phase solubility in many different substrates. These polymers may also be useful in supercritical CO<sub>2</sub> given that fluoropolymers are highly soluble in this medium.<sup>15</sup>



Polyelectrolytes are a well known class of polymers. While there has been some application of these polymers as supports for catalysts, this work has generally focused on using the a polycarboxylate as an anionic ligand.<sup>16</sup> We recently reported another approach to use of polyelectrolyte polymers in separation in homo- geneous catalysis.<sup>17</sup> In this approach, we used derivatives of a commercially available copolymer — Gantrez.

Gantrez (**2**) readily reacts with a phosphine-containing amine like bis(diphenylphosphinoethyl)amine to form an amic acid-containing polymer (**3**) (eq. 2). The resulting ligand has been



used to prepare cationic Rh(I) catalysts that are soluble in basic solutions (pH > 7.5) at catalytically useful concentrations of ca. 1 x 10<sup>-3</sup> M. Acidifying such solutions (CF<sub>3</sub>SO<sub>3</sub>H) produced an easily isolated yellow precipitate that readily redissolved when it is added to a fresh pH 7.5 solution. Recycling catalyst from an organic (CH<sub>3</sub>CN) solution was also feasible using solvent precipitation (addition into excess ether) to recover the polymer-bound catalyst at the reaction's end.



**SUMMARY**

The discussion illustrates the broad utility of polymers in separation and recovery of homogeneous catalysts. We have focused our attention on polymers like polyethylene, poly(alkene oxide)s, poly(*N*-isopropylacrylamide)s, fluorous polymers and amphoteric polymers. Other polymers too merit more attention.

**ACKNOWLEDGMENT**

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**IMPROVEMENTS IN PROCESS CHEMISTRY THROUGH CATALYSIS**

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Recent DuPont examples of improvements in process chemistry and catalysis will be described. These examples will illustrate how efficient chemical processes are inherently environmentally sound. The underlying principle which runs through these examples is the recognized need to address source reduction through sound chemistry rather than accepting waste treatment as inevitable.

## THE DEVELOPMENT OF GREEN OXIDANTS

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### ABSTRACT

Design strategies are presented for enabling an expanded use in homogeneous oxidation chemistry of nontoxic catalytic metal ions and natural primary oxidants such as hydrogen peroxide. The prototype metal-oxo systems that have been designed to arrange multiple reactions in time to achieve selectivity is described. Long-lived iron catalysts for the activation of hydrogen peroxide in water from pH 7 to 12 are presented in the context of their reactivity in bleaching organic dyes. This reactivity demonstrates the beginnings of our ability to control the lifetimes of catalysts that activate  $\text{H}_2\text{O}_2$  in water.

### INTRODUCTION

Chemists and Nature apply fundamentally different strategies to achieve selectivity. We chemists employ relatively simple design and attain selectivity by utilizing almost the entire periodic table. In contrast, Nature uses complex design such that selectivity can be accomplished with the comparatively small group of elements found in each local environment. In this strategic difference lies a root cause of much of the environmental damage attributable to chemistry. By employing a diversity of elements to control reactivity, chemists have been able to maneuver successfully in a comparatively simplistic design constellation. In the process, we confront local environments with elements from remote locations; often the unfamiliar elements are toxic in the local environment. As green chemistry develops, new technologies will emerge to replace elements that are uncommon in Nature with elements that are common.

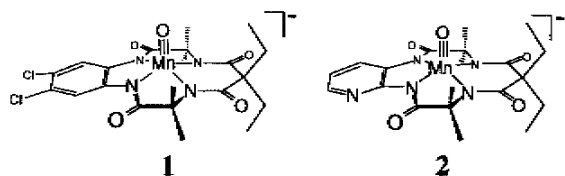
Oxidation chemistry is an area replete with green chemistry challenges<sup>1,2</sup> since it remains the least developed of the fundamental branches of reaction chemistry while at the same time it is extensively practiced in technologies fraught with environmental negatives. An important area concerns the development of homogeneous inorganic catalytic oxidation systems. Ideally, such systems would employ biologically common catalytic metals such as iron or manganese, and would involve activation in water of the biologically important oxidants, oxygen or hydrogen peroxide. By reflecting upon how Nature works in its strongly oxidizing enzymes, e.g., the monooxygenase or peroxidase systems, we can see that a master design strategy is employed and that this strategy is enabled by a series of design elements. Nature's master strategy is well-known; Nature constructs enzymes that speed up the desired reaction over potential competitors. Some of the design elements employed to achieve this include: (1) arrangement of the targeted transition state in space, (2) arrangement of multiple reactions in time; (3) priming of an enzyme with the substrate; (4) irreversibly expelling the product, (5) balancing metal-ligand combinations to control reactivity, and (6) employment of the repair and replacement mechanisms of life. It is interesting to reflect on the idea that the choice of the master strategy determines the need for design elements 1 and 6. The immense sophistication that results poses great difficulties for the transfer of Nature's oxidation design domain to technology. Therefore, identifying an alternative master strategy that can lead to technological systems constructed using natural design elements other than 1 and 6 would seem to provide hope for obtaining green oxidation systems. The master strategy that we are developing involves crafting catalytic systems not to speed up desired reactions, but rather to slow down all competing reactions. At the heart of the challenge is the requirement that one must produce a reactive catalytic oxidant that can oxidize a targeted substrate without attacking the other components of the system: the solvent, the primary oxidant, the ligands on the catalyst, the desired product.

We have devised an iterative design process for obtaining robust ligands and we have followed it for over fifteen years.<sup>3</sup> The process proceeds as follows. 1) A ligand system is designed that is thought might lead to oxidatively and hydrolytically robust complexes. 2) A metallocomplex of this ligand is produced and oxidized until ligand decay occurs. 3) The ligand degradation byproducts are fully identified, thereby revealing the ligand site that is vulnerable to oxidation and/or hydrolysis. 4) The reactive group is replaced with a substitute that it is thought will be more inert. 5) Steps 1 through 4 are repeated until complexes are obtained that are sufficiently resistant to

oxidative degradation to serve in desired catalytic roles. After numerous laps of the circle defined by these steps, we have arrived at ligand systems capable of supporting long-lived useful catalysts. Two subjects will be summarized in the remainder of this article. First, prototypical metal-oxo systems designed to arrange multiple reactions in time to achieve selectivity will be presented. Second, long-lived iron catalysts that activate hydrogen peroxide in water from pH 7 to 12 will be described in the context of their ability to bleach organic dyes.

### ARRANGING REACTIONS IN TIME TO ACHIEVE SELECTIVITY OBJECTIVES

Manganese  $Mn^V$  and  $Mn^{IV}$  oxo complexes of salen<sup>4,5</sup> and porphyrin ligands<sup>6,7</sup> have been proposed as the reactive intermediates in useful O-atom transfer processes. The  $Mn^V$ -oxo complexes **1**<sup>8</sup> was developed as the first oxidatively and hydrolytically stable manganyl. Unlike the porphyrin and salen systems, **1** and its related species were found not to be useful oxygen atom transfer agents. We assumed that the muted reactivity of **1** results from the higher negative charge and  $\sigma$ -donor capacities of the tetraamide ligands vis-a-vis the porphyrin or salen ligands. Thus, we chose to develop **2**, a system with a bidentate secondary site comprised of the pyridine-*N* and adjacent amide-*O* donors that can coordinate positively-charged ions in the immediate vicinity of its  $Mn(O)$  moiety to deliver an increase in O-electrophilicity over that of **1**. Complex **2** has been produced and characterized by many techniques, including an X-ray crystal structure.



The reversible formation of secondary complexes of **2** was monitored in acetonitrile by UV/Vis spectroscopy showing secondary ion binding to be significantly cation-dependent. Thus,  $Li^+$  binding exhibited isosbestic behavior and requires 2.5 equivalents of  $Li^+$  for complete lithiation,  $\log K_{25^\circ} = 5.02 \pm 0.06$ . It was similarly found that  $K^+$  does not bind to the secondary site, that  $Na^+$  binds twice (the binding second site is assumed to be one of the other three amide-*O* donors), and that multiply charged ions have high binding constants and bind more than one **2** when the latter is in excess. The considerable susceptibility of the manganyl moiety of **2** to secondary ion perturbation can be illustrated by the  $15\text{ cm}^{-1}$  blue shift of the  $\nu(Mn\equiv^{18}O)$  IR band (from  $939\text{ cm}^{-1}$  to  $954\text{ cm}^{-1}$ ) that occurs upon  $Li^+$  binding. This implies that  $Li^+$  binding induces a drop in the donor capacity of the macrocyclic tetraamido-*N* ligand to Mn, a drop that is compensated for by an increase in donation from the oxo ligand with an implied increase in its electrophilicity.

The effects of the different activating ions on reactivity were examined by studying a proof-of-concept oxidation, namely,  $Ph_3P$  to  $Ph_3PO$ . Relative rates in the presence of five equivalents of each secondary ion, normalized to the unactivated rate, were:  $Na^+ = 3$ ,  $Ba^{2+} = 5$ ,  $Mg^{2+} = 7$ ,  $Li^+ = 13$ ,  $Zn^{2+} = 24$ ,  $Sc^{3+} = 1244$ . As noted,  $Na^+$  ion is unique among the activating ions studied in possessing an appreciable second binding to **2** and  $K^+$  does not bind. No increase in the rate of  $Ph_3P$  oxidation was found upon changing  $[K^+]$  from 0 to 60 equiv, or upon increasing the activating ion:2 ratio from 5:1 to 60:1 for  $Mg^{2+}$  or  $Zn^{2+}$ . Small increases were found when this ratio increase was enacted for  $Ba^{2+}$  (1.2 fold),  $Li^+$  (2 fold) and  $Sc^{3+}$  (1.3 fold). In contrast, an increase in the  $Na^+$ :2 ratio from 5:1 to 60:1 produced a 169-fold increase in the rate of phosphine oxidation.

The reactivity of **2** as a *t*-butyl hydroperoxide activating catalyst was investigated with the electron-rich olefin, tetramethylethylene. A mixture of  $[Ph_4P]2$  (1 equiv),  $ZnTf_2$  (4.5 equiv), 2,3-dimethyl-2-butene (132 equiv), and TBHP (90%, 266 equiv) in  $CD_3CN$  was monitored at  $50^\circ C$  via  $^{13}C$  NMR until all of the olefin had been consumed (48 hr). The only observable product was 2,3-dimethylbut-3-en-2-ol (>98%, confirmed by GOMS). The disubstituted olefin of 2,3-dimethylbut-3-en-2-ol is not oxidized. The product, the generated *tert*-butanol, and the remaining TBHP had the same relative abundance; the reaction solution remained unchanged on standing for nine months. Thus, **2** presents a mild, selective and stable catalyst for O-atom transfers where the reactivity is attained by arranging more than one reaction in time to expand the reactivity of a system based on the environmentally desirable element, manganese.

### MASTERING CATALYST LIFETIMES FOR PEROXIDE ACTIVATION

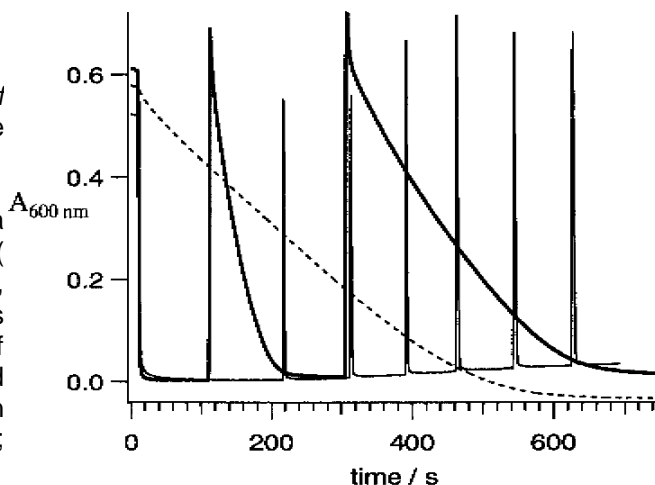
The catalytic activities of **3** and **4** in bleaching the organic dye pinacyanol chloride (PC) illustrate how ligand design can be used to control peroxide-activating catalyst lifetimes. In the experiments presented (Fig. 1), activator,  $H_2O_2$ , and buffer (pH 10) were combined and stirred in a quartz cuvette at  $25^\circ C$ . Then, aliquots of PC were added and the decrease in absorbance of the PC absorption band at  $\lambda_{max} = 600\text{ nm}$  ( $A_{600}$ ) was monitored as a function of time. Following bleaching of the first PC aliquots, additional aliquots (30 equiv relative to **3** or **4**) were added when the  $A_{600}$  had decreased to approximately 0. The two activators differ only in their respective

six-membered chelate rings; **3** contains a geminal dimethyl group while **4** contains a geminal diethyl group. Activator **3** has a much longer lifetime compared with **4**. With **4**, only one rapid bleaching cycle was achieved. By the time the fourth bleaching cycle was reached, only a small degree of enhancement over the background bleaching rate was observed, signaling that degradation of **4** was removing it from the catalyst pool. In contrast, after seven bleaching cycles (210 turnovers), bleaching remained extremely efficient for **3**; rapid dye oxidation could still be performed with **3** beyond one hour. Clearly **3** has a much longer lifetime than **4** as an activator for  $\text{H}_2\text{O}_2$  and this is attributed to the stronger C-H bond of the methyl (ca. 98 kcal mol<sup>-1</sup>) six-membered ring substituents of **3** versus the ethyl (ca. 95 kcal mol<sup>-1</sup>) substituents of **4**. Ligand degradation was shown to occur by attack at a C-H bond in this position.

### Acknowledgments

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**Figure 1.**  $A_{600 \text{ nm}}$  vs. time plot of the bleaching of a series of 12  $\mu\text{M}$  aliquots of pinacyanol chloride using (----) 0.0  $\mu\text{M}$  catalyst, single aliquot; (—) 0.43  $\mu\text{M}$  **3**, seven aliquots shown; (—) 0.43  $\mu\text{M}$  **4**, three aliquots shown. An \* denotes addition of a 12  $\mu\text{M}$  aliquot of pinacyanol chloride after the first bleaching reaction and a ‡ denotes addition of 4 mM  $\text{H}_2\text{O}_2$ . Reaction conditions: pH 10 (0.1 M  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ );  $T = 25^\circ\text{C}$ ; 4 mM  $\text{H}_2\text{O}_2$  initially, 4 ppm Dequest 2066.



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# **ZEOLITES**



## ZEOLITE TECHNOLOGIES FOR A GREENER ENVIRONMENT

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### INTRODUCTION

Applications using aluminosilicate and other composition zeolites are undergoing intensive development and commercialization due to their process and environmental advantages. Due to their diverse properties, these materials are finding applicability in a broad range of industrial processes that are environmentally sensitive. A review of the properties of zeolites and how these properties are useful for extension into the environmental areas will be given and an explanation of some of the green application areas for which zeolites are being investigated will be discussed.

### ZEOLITE PROPERTIES AND APPLICATION AREAS

Molecular sieve zeolites are a class of stable mineral and synthetic crystalline inorganic compounds characterized by the presence of an open oxide three dimensional framework structure. This open structure leads to a regular network of uniform pores of specific molecular dimensions. The porous structure enables the zeolites to selectively admit some molecules while excluding those that are too large to fit into the pores; this leads to its molecular sieve properties. In commercial materials, the framework is generally an aluminosilicate one in which the aluminum and silicon atoms are tetrahedrally coordinated through oxygen atoms in a continuous array. The framework charge deficiency resulting from the tetrahedral coordination of the aluminum atoms is balanced by cations which are not an integral part of the framework. These cations have a high degree of mobility and are exchangeable; the type of cation present and the number effect the catalytic, adsorptive and ion exchange properties of the zeolites.

The main application areas of zeolites use different aspects of their chemistry. In the area of ion exchange, zeolites can be considered to be the support for mobile, nonframework cations; the largest volume application use of zeolites is as water softeners in detergents. As sorbents and molecular sieves, the aluminosilicate zeolites are hydrophilic and are widely used as desiccants and adsorbers of polar molecules for separation and purification. The highly siliceous zeolites have frameworks that are close to neutral and organophilic, and they have found use as adsorbers of organic molecules such as odors. In catalysis, zeolites display highly active sites and shape selectivity, and they are used extensively in the petroleum and petrochemical industries.

### ZEOLITE USE IN CLEANER TECHNOLOGIES

The drivers for cleaner technologies are numerous and interwoven, and they include regulatory pressures, economic considerations and social concerns. The regulations and laws of many countries are becoming increasingly more stringent requiring a marked decrease in effluents, wastes and by-products; fines and possible shut downs are penalties that are faced for non-compliance. Increased legislation of processes frequently results in an increase in costs for a manufacturer. These economic considerations are driving companies to devise new cheaper methods to produce materials in order to compete with third world countries that do not face legislative pressures to change production methods. Social issues centering on the desire for a clean environment are driving consumers to demand that materials be produced in a socially conscious manner.

It is recognized that the obvious (and inexpensive) solutions to many pollution problems have been investigated and that more creative technologies will be needed in the future to meet the increasing regulatory push to eliminate or treat effluents. The unique properties and selectivities of zeolites provide effective solutions for environmental pollution by minimizing the production of pollutants and by secondary treatment of the effluents produced. Among the areas where zeolites have been studied are in air cleanup such as: stationary and mobile source deNO<sub>x</sub>, deVO<sub>x</sub> and deSO<sub>x</sub>, automotive cold start; in land and wastewater cleanup; in fine chemical process improvement such as: waste minimization, higher efficiency, cheaper feedstocks. Several of these areas will be covered in the talk with specific examples, including:

Atmospheric Gases: The reduction of NO<sub>x</sub> in the atmosphere has been a major thrust of the Clean Air Act. NO<sub>x</sub> is produced by both mobile sources such as cars and by stationary sources such as power plants. In the mobile sources, gasoline engines use a precious metal catalyst; however, in diesel automobiles metal exchanged zeolites have been employed especially in the European and Japanese markets<sup>1</sup>.

In the stationery market, metal ion exchanged zeolites have been utilized both with and without a hydrocarbon reductant. A hybrid technology of zeolites and SCR has been developed in which ammonia is the reductant<sup>2</sup>. In NO<sub>x</sub> reduction, the zeolite must be able to withstand high temperatures and high space velocities; frequently, the stream is very acidic and contains particulates and metals that can poison the zeolite.

Volatile organic chemicals (VOCs) are defined by the US EPA as stable products exhibiting a vapor pressure above 0.1 mm Hg at normal temperature and pressure. Based on that definition, these materials are found in almost every area of the chemical industry and include: alcohol,s, ketones, aldehydes, aromatics, halogenated hydrocarbons; they can be toxic, carcinogenic, irritating and/or flammable. In addition to the health problems that they may present, they are regulated due to their involvement in the photochemical formation of smog. Reduction or suppression of VOCs can be achieved by recovery and reuse, by thermal destruction or by the combination of recovery/concentration and destruction. Adsorption of VOCs can be done on a variety of materials such as carbons and silicas, and these materials are quite efficient in high VOC concentration streams. However, dilute streams are becoming increasingly more regulated, and there is a need for a material that is more selective; high silica, hydrophobic zeolites such as ZSM-5 types and dealuminated faujasites are very effective in this application, especially in streams with high relative humidity.

Automotive Cold Start: As the regulations for cars approach ZLEV (zero level emission vehicles), reduction of the amount of emissions produced during the first two minutes will be required. During this period while the catalyst is reaching light-off or effective operating temperature, the emissions produced are released into the atmosphere and can account for more than 60% of the hydrocarbon emissions of the engine. One method of controlling these emissions is by trapping them on an adsorbent and then releasing them when the catalyst is at the proper temperature<sup>3</sup>. This hydrocarbon trap can utilize a zeolite that has the ability to adsorb small organic molecules in the presence of water and retain them for up to two minutes at increasing temperature. The zeolite must also be able to tolerate temperature excursions of up to 1000 °C and retain capacity. Several companies have recently announced hydrocarbon traps that use zeolites<sup>4</sup> and that are effective at controlling the emissions to below the US 2000 emissions requirement.

Wastewater Cleanup: The cleanup of wastewater produced by industry is another major thrust of the EPA. The removal of chlorinated hydrocarbons (CHCs) is one example; regulations require that aqueous stream effluent concentrations be below 3 ppm depending on the CHC. This will require lowering the concentrations from saturation levels and the methods used for the water purification will be based on air or steam stripping followed by adsorption. Adsorption on carbon or polystyrene resins has been used commercially<sup>5</sup>, however, in-situ regeneration on a large scale has limited the use. High silica zeolites are drawing increasing attention as potential adsorbents in this application.

Fine Chemical Process Improvements: The fine chemical industry is generally defined as the selective production of organic compounds containing functional groups. Traditionally, many of these processes have been homogeneous, liquid catalyzed systems that generate large quantities of waste during the neutralization process including contaminated water streams, salts and heavy metals. These materials make the work up costly and can lead to corrosion problems and increased costs. Zeolites are being extensively studied as heterogeneous catalysts that can be recovered and recycled more easily and cheaply leading to less waste and fewer by-products<sup>6</sup>. The cost of the materials is cheaper and the processes are more efficient, frequently combining all of the reactants in one pot. Zeolites also are more selective in comparison to classic synthetic paths.

Cheaper Feedstocks: One area of environmental improvement that must be undertaken is the use of cheaper feedstocks including biomass. One excellent example of the use of zeolites in this application is the Mobil methanol to gasoline (MTG) process<sup>7</sup> that has been commercialized in New Zealand. In this process, zeolites are used to convert the methanol that can be obtained from coal, natural gas or biomass to liquid fuel or chemical feedstocks. Additional areas of interest that could include the use of zeolites are the production of syncrude from flare gases at refineries and the upgrade of CO<sub>2</sub> to valuable products.



## CONCLUSIONS

The many different types of zeolites available and their unique properties are extending their use into new and exciting areas. In the catalysis area, the properties of high acidity, shape selectivity and support for active materials have found use in areas requiring more environmentally friendly catalysis. The ever extending range of zeolite properties from hydrophilic to hydrophobic is allowing their use as organophilic adsorbents in areas where traditional adsorbents such as carbon cannot be used: low concentration streams, high temperature and high humidity conditions. Zeolite properties such as regenerability, thermal stability and tunable acidity allow them to be tailored for various applications. Their ability to be formed into different shapes that are compatible with many reactor designs.

The need for new step-out materials and processes that will help to solve the environmental problems of tomorrow are expanding the research that is being done on zeolites, and they are becoming increasingly the material of choice for many of the application areas that are being investigated in order to assure that green chemistry becomes the standard for production in the years to come.

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## SELECTIVE PHOTOOXIDATION OF HYDROCARBONS IN ZEOLITES USING VISIBLE LIGHT

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## ABSTRACT

Selective photooxidation of hydrocarbons in zeolites with visible light is being explored as an environmentally benign alternative to conventional liquid phase oxidation of industrially important chemicals. The goal of our work is to demonstrate that selective photooxidation in zeolites with visible light is a general technique and that synthetic strategies can be developed using the shape-selective and chemical properties of different zeolites. We have studied the photooxidation of hydrocarbons with visible light in BaX, BaY and BaZSM-5 using FTIR, UV/Vis diffuse reflectance and solid state NMR. Preliminary FTIR results suggest that selective photooxidation of propylene to acrolein with visible light occurs in BaX, BaY and BaZSM-5. Further work is in progress to extend these results to other hydrocarbons and other zeolite hosts.

## INTRODUCTION

Recently, Frei and coworkers have demonstrated that hydrocarbons in zeolite Y can be selectively oxidized by visible light.<sup>1-7</sup> The basis for the selectivity is the hydrocarbon•O<sub>2</sub> charge transfer state that is formed in the zeolite after photolysis. The hypothesis is that the electrostatic field of the zeolite stabilizes the charge transfer state and the use of visible rather than ultraviolet light allows access to low energy pathways, eliminating many secondary photoprocesses and leading to the remarkable selectivity.<sup>7</sup> The geometric constraints of the zeolite framework are also important to the selectivity. The implications of this methodology for environmentally benign synthesis of chemicals are twofold. The increased selectivity of the oxidation reaction will decrease the production of unwanted side products. In addition, a zeolite catalyst and gas phase reactants and products will eliminate the use of expensive and environmentally toxic solvents.

The focus of this study is to demonstrate that selective photooxidation in zeolites is a general technique and that synthetic strategies can be developed using the shape-selective and chemical properties of different zeolites.

Using FTIR(Fourier Transform Infrared) spectroscopy, we have investigated the photooxidation of propylene to acrolein with visible light in three different zeolites - BaX, BaY and BaZSM-5. Selective photooxidation of propylene in BaY has been reported by Frei and coworkers,<sup>5</sup> but has not previously been reported in other zeolites.

## EXPERIMENTAL SECTION

Zeolites BaY, BaX and BaZSM-5 were prepared from NaY (Aldrich), NaX (Acros Organics) and NaZSM-5 (Zeolyst) by standard ion-exchange procedures using aqueous BaCl<sub>2</sub> solutions.<sup>5</sup> The degree of ion-exchange was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The Si/Al and Ba/Al ratios for the samples used in this study are: BaX (Si/Al = 1.4, Ba/Al = 0.33), BaY (Si/Al = 2.9, Ba/Al = 0.53) and BaZSM-5 (Si/Al = 19, Ba/Al = 0.26).

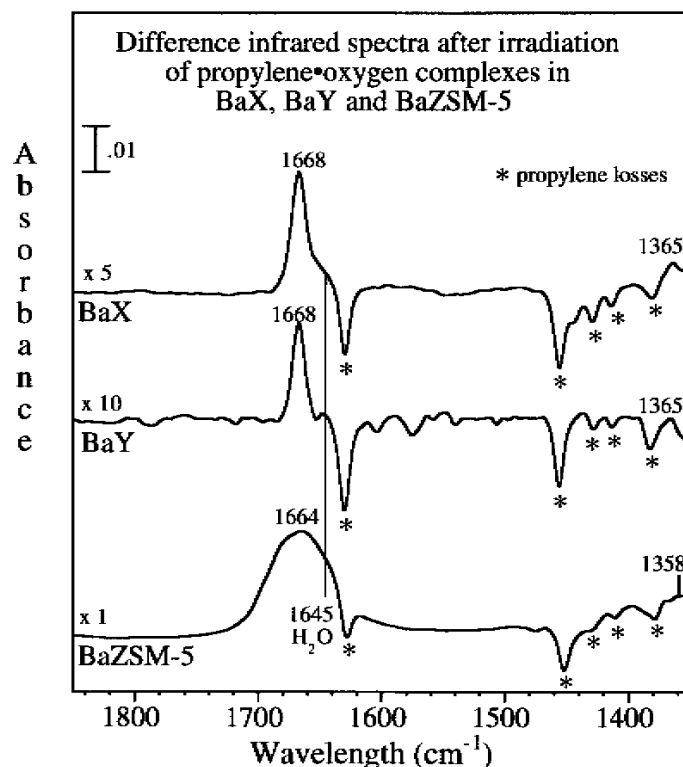
Fourier Transform Infrared (FTIR) spectra were recorded with a Mattson RS-10000 equipped with a narrowband MCT detector. The IR cell has been described previously.<sup>8,9</sup> The zeolite is sprayed from a water slurry onto a photo-etched tungsten grid held at 40°C. The tungsten grid is held in place by a set of Ni jaws and is used to heat the samples. The temperature is measured by a thermocouple wire attached to the tungsten grid. The entire assembly is mounted inside of a 2 3/4" stainless steel cube which can be evacuated by a turbomolecular pump to a pressure of  $1 \times 10^{-7}$  torr. Each spectrum was recorded by averaging 1000 scans with an instrument resolution of 4 cm<sup>-1</sup>. An Oriel mercury lamp (500 W) equipped with filters was used as the primary light source for photolysis of the samples.

The zeolites were pretreated by heating overnight under vacuum to 200°C (BaX, BaY) and 350°C (BaZSM-5) to remove water from the samples. Propylene (Matheson; 99.6%) was introduced into the IR cell at a pressure of approximately 25 torr and allowed to equilibrate for one hour. Gas phase propylene was pumped out. Next, 750 torr of molecular oxygen (Air Products; 99.6%) was added to the IR cell and the system was allowed to equilibrate for 1.5 hours. The sample was irradiated with  $\lambda > 490$  using a 490 nm broadband filter (Oriel 59492) on the output of the lamp. The lamp power at the sample was 89 mW/cm<sup>2</sup>.

## RESULTS AND DISCUSSION

Figure 1 shows the FTIR difference spectra of the products observed after photolysis of propylene and oxygen loaded in BaX, BaY and BaZSM-5. The difference spectra were obtained by spectral subtraction of the spectrum recorded prior to irradiation and the spectrum recorded after irradiation.

**Figure 1.** Difference spectra following one hour of broadband irradiation ( $\lambda > 490$  nm) of propylene•O<sub>2</sub> complexes in zeolites BaX, BaY and BaZSM-5. Acrolein is the sole hydrocarbon product in all three zeolites. Propylene losses are indicated by asterisks.



For BaX and BaY, prominent product bands are observed at 1668 and 1365 cm<sup>-1</sup> and are assigned to acrolein. Loss of propylene is evidenced by the negative peaks labeled with asterisks. The results for BaY are consistent with the previous work of Frei and coworkers who observed similar acrolein product bands.<sup>5</sup> These results are not surprising given the similarities in the structure and properties of zeolites X and Y. Zeolites X and Y have the same faujasite structure but differ in silicon to aluminum ratio of the framework. Zeolite Y typically has a Si/Al ratio ranging from 2-5 while zeolite X has a Si/Al ratio ranging from 1-1.5.<sup>10</sup>

The third zeolite to be evaluated for propylene photooxidation was BaZSM-5. The structure and chemical composition of ZSM-5 are very different than zeolites X and Y. ZSM-5 has intersecting channels with pore diameters of approximately 5.4 - 5.6 Å and a Si/Al ratio of greater than 15.<sup>10</sup> The FTIR spectrum of the photolysis

products after propylene photooxidation in BaZSM-5 is shown in Figure 1 (bottom spectrum). Major peaks at 1664 and 1358  $\text{cm}^{-1}$  are observed. These two bands match the FTIR bands observed when acrolein is adsorbed on BaZSM-5. In general, the infrared bands of hydrocarbon products adsorbed in BaZSM-5 are broader than those observed in BaX and BaY. Water is also formed as a product of the reaction as indicated by a shoulder at 1645  $\text{cm}^{-1}$  in the spectrum.<sup>11</sup> At shorter wavelengths,  $\lambda < 490$  nm, both formaldehyde (major peak near 1703  $\text{cm}^{-1}$ ) and  $\text{CO}_2$  (2352  $\text{cm}^{-1}$ ) form in BaX, BaY. For BaZSM-5, a small amount of  $\text{CO}_2$  is also formed at the longer wavelengths suggesting a possible loss of selectivity in this reaction. The oxidation products formed in BaZSM-5 are easily removed by heating the zeolite to moderate temperatures ( $> 200^\circ\text{C}$ ).<sup>12</sup> This has potentially important implications for the feasibility of commercial application of photooxidation in zeolites; since the products are strongly bound and difficult to remove from the zeolite at ambient temperature.<sup>7</sup>

The selectivity of this oxidation reaction for the aldehyde product is due to the electric field gradient of the zeolite host.<sup>7</sup> In order to develop a fundamental understanding of this selectivity, we have initiated experiments to determine the electrostatic field inside BaX, BaY and BaZSM-5. Vibrational spectroscopy of probe molecules such as  $\text{N}_2$ , CO and  $\text{H}_2$  has been used to evaluate local electric fields in zeolites.<sup>13-15</sup> In particular, the frequency of adsorbed CO can blue shift by as much as 40  $\text{cm}^{-1}$  due to changes in the electric field around the probe molecule. Pacchioni et al. have carried out quantitative calculations of the shift in CO vibrational frequency as a function of the strength of the electric field along the axis of the adsorbed CO molecule.<sup>14</sup> Using observed CO stretching frequencies from experimental FTIR measurements, we have calculated the electric fields in BaX, BaY and BaZSM-5 samples.<sup>16</sup> A CO vibrational frequency in BaZSM-5 of 2184  $\text{cm}^{-1}$  corresponds to an electric field of 7.4  $\text{V nm}^{-1}$  in the vicinity of the exchangeable cation. CO vibrational frequencies of 2170  $\text{cm}^{-1}$  in BaX and 2171  $\text{cm}^{-1}$  in BaY correspond to electric fields of 4.8 and 5.0  $\text{V nm}^{-1}$ . These values are the same order of magnitude as measured by Frei and coworkers for BaY using  $\text{N}_2$  as a probe molecule<sup>7</sup> suggesting that BaX and BaZSM-5 also have field gradients that are sufficient to permit photooxidation of hydrocarbons with visible light. UV/Vis diffuse reflectance experiments are currently underway to measure the charge transfer absorption bands of hydrocarbon $\cdot\text{O}_2$  charge transfer complexes in BaX, BaY and BaZSM-5.

## SUMMARY

We have demonstrated that selective photooxidation of propylene to acrolein by visible light is observed in BaY, BaX and BaZSM-5. The ability to exploit zeolite hosts with different chemical properties and shape selectivities has important implications for potential industrial applications. The electric field gradient and possibly the selectivity can be changed by varying the exchangeable cation. Studies to measure electric field gradients and charge transfer absorption bands are in progress. These results will be used to guide the development of systems for the selective photooxidation of hydrocarbons.

## ACKNOWLEDGMENTS

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## CATALYSIS BY STRONG SOLID ACIDS

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Acid catalysis is a critical component in octane enhancement processes such as isomerization and alkylation, which lead predominantly to highly branched isoparaffins with high octane. Isomerization and alkylation processes in current practice rely on liquid acids (e.g., H<sub>2</sub>SO<sub>4</sub>, HF, H<sub>3</sub>PO<sub>4</sub>) and on halogen-promoted metal oxides (HClAl<sub>2</sub>O<sub>3</sub>, HF-Al<sub>2</sub>O<sub>3</sub>). These materials pose significant corrosion, containment, and environmental challenges that can be overcome by using metal oxides. Many syntheses of fine chemicals and pharmaceutical precursors require acylation and alkylation reactions that use halogen-containing catalysts, stoichiometric reagents, or mineral acids. As the use of halogens in chemical processes becomes increasingly restricted and as waste disposal costs increase, processes using solid acid catalysts based on metal oxides must gradually replace current technologies. Stronger incentives for replacing current processes emerge when the selectivity and stability of these solid acids exceed those currently obtained with mineral acids and AlCl<sub>3</sub>. Then, energy and atom efficiency will concurrently improve as toxic and corrosive materials are removed from chemical synthesis processes.

Ipattief and Pines first prepared solid acids as catalysts in 1940 for isomerization and alkylation reactions leading to high octane fuels. These catalysts consisted of diatomaceous earths impregnated with phosphoric acid. Currently, about 80 types of chemical processes use about 100 solid acid compositions within the refining, petrochemicals, and pharmaceutical industries<sup>1</sup>. In general, these solid catalysts have replaced liquid catalysts and stoichiometric reagents for both environmental and economic reasons. Significant progress in the synthesis of solid acid materials with controlled pore and site structures has occurred within the last decade, but some formidable challenges remain in order to extend the use of solid acids to other refining and chemical processes. Solid acid catalysts tend to have lower site densities than their liquid counterparts and acid sites tend to be "protected" within constrained pore structures. As a result, accessibility to reactants and removal of products before undesired secondary reactions, such as deactivation, become difficult. The recent development of ordered mesoporous solids<sup>2</sup>, large-pore "zeolites"<sup>3</sup>, and molecular oxide clusters supported on mesoporous oxides<sup>4,5</sup> represent significant recent progress towards overcoming some of these challenges.

Restricted channels within microporous (zeolitic) solids contain strong acid sites of uniform structure protected within a shape-selective environment that can inhibit side reactions and deactivation. Mesoporous solid acids consisting of ordered tubules or random agglomerates of metal oxides provide a more open environment for catalytic reactions in which reactive intermediates are the desired products. Recent advances in the design of microporous structures, in the selective placement of isolated cations within such structures, and in the synthesis of supported oxide nanoclusters have led to selective acid catalysts for complex reactions requiring multifunctional surfaces and controlled site structures. Chemoselective isomerization<sup>5</sup> alkylation<sup>6</sup> and acylation<sup>7</sup> and stereoselective hydrogen transfer reactions<sup>8</sup> that previously required liquid acids or halogen-containing solids have been recently reported to occur with improved selectivity and lessened environmental risk on supported oxide clusters and on microporous structures containing Bronsted or Lewis acid sites. In addition, new reactions, such as chain-limited alkane pyrolysis to form C<sub>6</sub>-C<sub>8</sub> aromatics, appear to occur when conventional microporous structures containing acid sites are modified by the presence of redox sites located at cation exchange sites<sup>9</sup>.

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# BIOCATALYSIS





**BIOCATALYSIS FOR ENVIRONMENTALLY FRIENDLY POLYMER SYNTHESIS**

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The exquisite selectivities and fast catalytic rates of enzymes under ambient conditions provide commercially competitive alternatives to traditional organic synthesis to be developed in many diverse areas including oxidoreductions, condensations, among others. Nowhere is this more evident than in the use of biocatalysis for the synthesis and modification of polymers. It is difficult to believe that enzymes can compete with chemical catalysts for the production of polymers. In most respects, enzymes appear poorly suited to function as effective catalysts in this area due to the high productivities required for economical production of polymers. The past several years has seen dramatic growth in the application of enzymes for polymer design and modification. Enzymes offer significant advantages over chemical catalysts for the synthesis of materials with highly specialized properties including biodegradability, biocompatibility, inherent selectivity (e.g., enantio-, regio-, and chemo-), and easily tailored functionalities all produced under conditions that minimize the formation of byproducts and the avoidance of unwanted pollutants. In particular, polyfunctional monomers and precursors provide challenging problems in the use of traditional catalysis as reaction stoichiometry, and hence polymer molecular weight and physicochemical properties, is controlled by catalyst selectivity. An increasing number of novel materials are synthesized from polyfunctional precursors. These materials include chiral polymers, photo-optical materials (e.g., to provide control of refractive index), and biodegradable/biocompatible polymers. Highly selective (e.g., regio-, stereo-, and chemo-) syntheses are often required for suitable polymeric properties. Specific examples of this requirement are the synthesis of water-absorbent, biocompatible/biodegradable polymers from sugars and the synthesis of phenolic- based redox polymers. In both instances, the biological reactant is multifunctional and are well-suited for enzymic modification as opposed to chemical synthesis. Moreover, the use of biocatalysts results in an environmental impact due to a reduction in byproduct (often waste) yield and ability to utilize environmentally-benign raw materials.

Our research has focused on unique enzymatic transformations, often coupled to chemical steps, to prepare polymeric materials with unique and functional structures and chemistries. A variety of complex, yet environmentally appealing, raw materials can be used (examples are shown in Fig. 1) for incorporation into novel materials with unique structures and properties. For example, linear sugar-based poly(acrylate)s have been prepared that have  $M_n$  as high as 2,400,000. We have also prepared crosslinked sugarbased hydrogels that swell in water over 1000-times their weight. These gels are nonionic and are relatively unaffected by pH and ionic strength. These materials are also partially biodegradable - the sugar pendent groups are easily hydrolyzed by extracellular enzymes. The biocatalytic process involves the use of enzymes in organic solvents to catalyze the acylation of sugars with acrylic esters. As opposed to the use of hazardous solvents, we perform the enzymatic reaction in bulk acyl donor (Fig. 1), thereby maximizing enzyme reactivity and conversion, and eliminating the use of non-essential organic solvents such as pyridine. The polymerization takes place chemically via free radical initiation in aqueous solutions and takes advantage of the high solubility of sugar acrylates in water (Fig. 2).

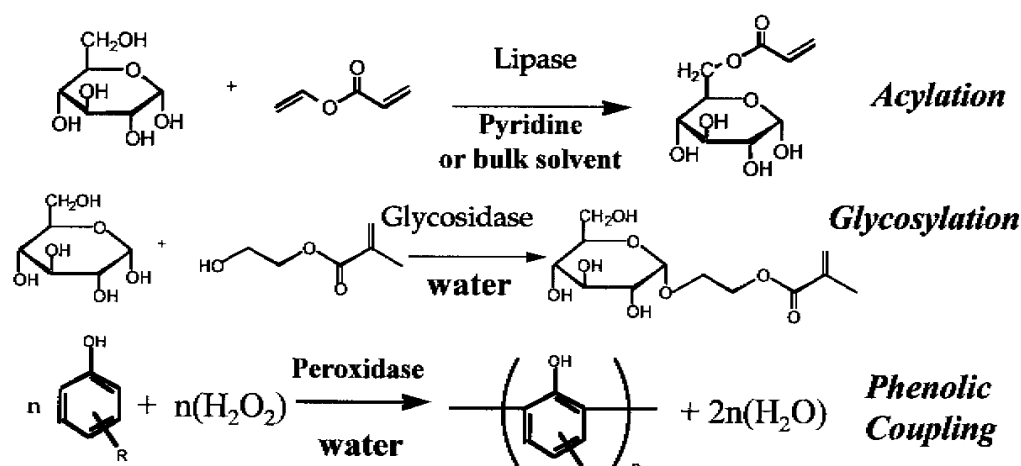
We have also focused on phenolic-based polymers that have redox chemistries, and using a biocatalytic approach in aqueous solutions to perform the synthesis. Specifically, we have developed a bienzymic approach to the synthesis of poly(hydroquinone). The first enzyme,  $\beta$ -glucuronidase from bovine liver, catalyzes the selective blocking of a single hydroxyl group on hydroquinone and this is followed by peroxidase (either from horseradish or soybean) catalyzed oxidation of the hydroquinone glycoside to poly(arbutin) (Fig. 3). Acid hydrolysis of poly(arbutin)s with  $M_n$ 's approaching 3200 leads to poly(hydroquinone)s containing up to 12 repeat units. The poly(hydroquinone)s produced were highly stable and had the same redox potentials as hydroquinone as determined by cyclic voltammetry. No change in redox potential is observed after 500 cycles. The highly selective nature of enzymatic catalysis leads to a poly(hydroquinone) structure that is distinct from the electrochemically prepared polymer and contains highly symmetric links between the hydroquinone moieties. This provides increased solubility in organic solvents.

The combination of enzyme technology with polymer chemistry has opened the door to the development of "biocatalytic plastics". These materials have enzymes incorporated into the polymer networks of plastics to

provide highly active and stable biocatalysts. Enzyme-containing polymeric materials show high activity and stability in both aqueous and organic media. Specifically, plastics containing  $\alpha$ -chymotrypsin and subtilisin Carlsberg, can contain up to ca. 50% (w/w) total protein in plastic materials such as poly(methyl methacrylate, styrene, vinyl acetate, and ethyl vinyl ether). The activation achieved in organic solvents by incorporating proteases in plastic matrices allows for the efficient synthesis of peptides, and sugar and nucleoside esters. For example, rate enhancements over the lyophilized, suspended chymotrypsin for peptide synthesis of over 2,000-fold are obtained in isooctane and over 13,000-fold are obtained in THF. The marriage of enzyme technology with polymer chemistry opens up a tantalizing array of unique applications for "plastic enzymes", including active and stable biocatalysts in paints, coatings, resins, foams, beads, as well as membranes, fibers, and tubings. Such plastic enzymes can also have a significant impact on waste reduction in chemical processes as the matrices result in enzymes with high activity in environments leading to high productivity. This, in turn, results in the use of less solvents and fewer byproducts than both traditional chemical synthesis and biocatalysis, the latter often requiring rather poorly active enzymes.

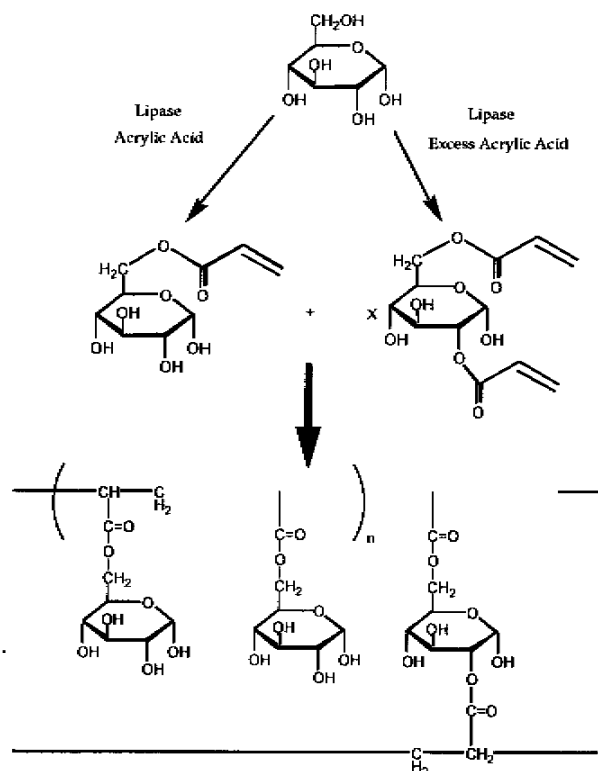
### Polymers Are Built Upon Monomers and Linkages

Reactions in organic solvents are needed to utilize the power of enzymes for polymer synthesis — Complex monomers coupled with relevant linkages

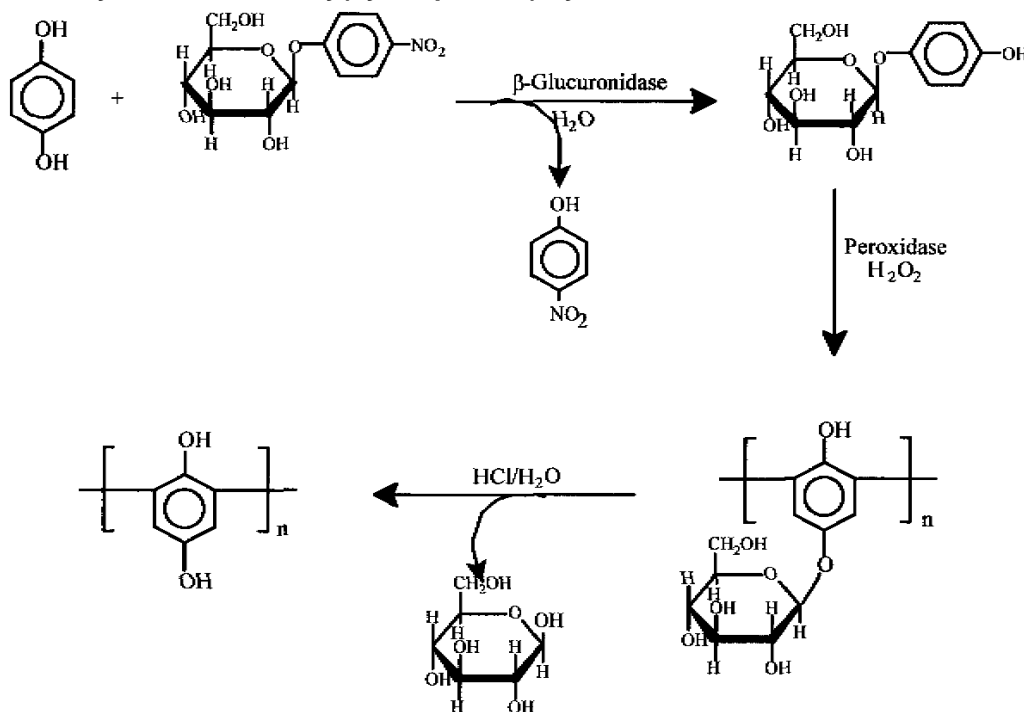
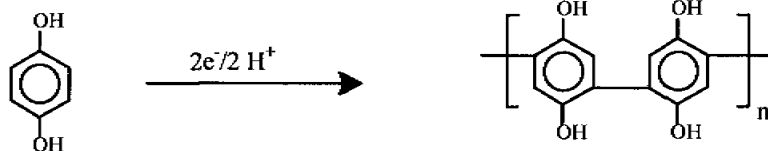


**Figure 1.** Monomers and enzyme-catalyzed conversions for use in environmentally-friendly polymer synthesis.

### Crosslinked Hydrogel Preparation



**Figure 2.** Preparation of sugar-based hydrogels.

**Multienzymic Route to Poly(hydroquinone) Synthesis****Electrochemical Synthesis of Poly- (hydroquinone)**

**Figure 3.** Coupled enzymatic synthesis of poly(hydroquinone) compared to the electrochemical route.

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**NATURAL CATALYSTS AND GREEN SOLVENTS: A WINNING COMBINATION FOR THE ENVIRONMENT**

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The remarkable specificity and activity of enzymes has led to a resurgence of interest in their use as catalysts for chemical synthesis. Of particular note is work over the last decade which has demonstrated that enzymes function effectively in a wide variety of environments, including nonaqueous solvent. The ability to remove the necessity for water in a chemical process environment enables the integration of enzymes in synthetic processes, including those directed at polymerization. There has been an equally strong interest in the replacement of organic solvents with the benign, nonregulated, tunable solvent, supercritical carbon dioxide. This talk will describe the use of enzymes in polyester synthesis as an example of the power of biological approaches to waste minimization. In addition, the use of a supercritical solvent and an enzyme to synthesize unique polyesters will be described to demonstrate what can be achieved when one combines these green strategies.

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### **SOYBEAN PEROXIDASE AS AN INDUSTRIAL CATALYST**

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Recently, a process to cost effectively isolate peroxidase from soybean seedcoats has been developed in our laboratories. Soybean seed coats are a commodity product and are available year round in North America in large volumes. Most dramatically, the useful operational temperature for the soy peroxidase is 40° C higher than for horseradish peroxidase resulting in shorter reaction times and greater reactor efficiency. The soy peroxidase can be utilized in processes to make a wide variety of chemical intermediates traditionally made using high temperature caustic fusion, as well as formaldehyde-free phenolic resins. The chemical intermediates are used in the production in a broad range of products including antioxidants, photoresists, UV absorbers, liquid crystal polymers and epoxies. The soy peroxidase based process used to manufacture resins and chemical intermediates will be described.

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# HETEROGENEOUS



## CLEAN COMBUSTION CATALYST CHALLENGES FOR THE 21 CENTURY

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### ABSTRACT

Catalyst challenges for cleaning the environment in the 21st century are outlined. Catalysts to decompose and/or reduce NO<sub>x</sub> with on-board derived fuels is an enabling technology for the development of clean, fuel efficient lean burn gasoline and diesel engines. Gasoline powered fuel cells for vehicular applications is targeted for wide scale by 2015. The introduction of catalytic combustion will revolutionize power generation with ultra low emissions and enhanced fuel economy.

### INTRODUCTION

The last 25 years of the 20th century has resulted in significant reductions in emissions from mobile and stationary combustion sources<sup>1</sup>. Since the enactment of the Clean Air Act in 1970, and its amendments in 1990, hydrocarbon (HC), carbon monoxide (CO), nitric oxides (NO<sub>x</sub>) and particulate emissions from the combustion of gasoline and diesel fuels have been dramatically reduced. Similarly reductions from power plants, stationary engines, small appliance engines, etc, have been also been realized. The solution has been a combination of engine control technology and advanced catalytic materials operating in concert. The catalyst is now the heart of many combustion systems and allows the engine manufacturer much flexibility in engine design.

As we approach the 21st century the momentum for further reductions in harmful emissions will continue but the need for improved fuel economy and reduction in green house gases must be addressed. Once again the catalyst is expected to play a vital role in meeting these new challenges.

### MOBILE-SOURCES: GASOLINE AND DIESEL FUELED ENGINES

Lean combustion for gasoline fueled vehicles will increase fuel economy by up to 25% and decrease CO<sub>2</sub> by a similar amount. Fuel efficient lean burn engine technology is moving forward at a rapid pace but to continue further reductions in emissions the development of a catalytic technology for the decomposition or reduction of NO<sub>x</sub> (NO or NO<sub>2</sub>) in the exhaust is essential. Current three way catalysts (TWC) are highly efficient for catalytically oxidizing HC and CO in lean environments but not for NO<sub>x</sub>. Ideally it is desirable to have a catalyst which passively decomposes NO<sub>x</sub> at high rates with sufficient durability for the life of the engine according to reaction (1).



Research efforts for the past 15 years have failed to invent a catalyst so scientists and engineers have turned to an alternative approach of reducing NO<sub>x</sub> with on-board derived hydrocarbons as shown in reaction (2).



Although somewhat more successful than for decomposition catalysts no materials with sufficient activity over the temperature ranges required have been found. The absence of HC/NO<sub>x</sub> selectivity of reaction (2) is due to reaction (3) which dominates for Pt catalysts at temperatures above about 250°C.



Other catalyst candidates, such as Cu/ZSM-5, are active above 400 °C but suffer from poor thermal stability and deactivate by SO<sub>x</sub> always present in the exhaust of gasoline and diesel engines<sup>2</sup>.

Therefore, a highly selective and durable lean NO<sub>x</sub> catalyst is an enabling technology for further improvements in engines with enhanced fuel economy and reductions in toxic emissions. New ideas in engine control and catalytic materials will be needed well into the 21 century.

### MOBILE SOURCES: GASOLINE FUEL CELLS

Fuel cells are electrocatalytic devices which convert chemical energy directly into electricity with high efficiency and without generation of primary pollutants. It was this technology that powered our space missions. The fuel

cell has been identified by the major automobile manufacturers as one promising approach for powering vehicles to meet the Partnership for a New Generation Vehicle (PNGV) objectives of producing a 80 mpg vehicle with near zero emissions. Hydrogen is oxidized at a Pt electrocatalyst anode and oxygen (from air) reduced at a Pt cathode. The two half cell reactions (4) and (5) produced water as the net chemical product (6) and electricity.



Since the availability of  $\text{H}_2$  for convenient refueling is non-existent and the infra-structure requirement cost prohibitive Chrysler has announced their goal of developing a vehicle powered by a fuel cell using on-board gasoline as the source of  $\text{H}_2$ . The generation of clean  $\text{H}_2$  for chemical production has existed for many years and Chrysler, in conjunction with Delphi (division of GM), intends to adapt this technology for passenger cars<sup>3</sup>.

Gasoline is composed primarily of paraffinic and aromatic hydrocarbons with carbon numbers between 8 and 10. It can be converted with limited amounts of  $\text{O}_2$  to  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$  and  $\text{CO}_2$  according to the partial oxidation (POX) reaction (7).



The well known catalytic water gas shift reaction generates more  $\text{H}_2$  by the reaction of  $\text{CO}$  and  $\text{H}_2\text{O}$  (8)



Residual  $\text{CO}$ , which poisons the Pt electrocatalyst, is selectively oxidized (9) by addition of a stoichiometric amount of  $\text{O}_2$ , without oxidizing the large excess of  $\text{H}_2$  present (10)



The system will require complete process integration for heat management for efficient operation.

In the last 10 years the price of the fuel cell power plant relative to a gasoline engine has decreased from 1000 to 10 so further cost reduction is a reasonable challenge. Reductions in the amount of Pt electrocatalyst needed will significantly impact the attainment of this goal. Projections by Chrysler are for wide scale commercial use by 2015.

## STATIONARY POWER GENERATION

Power plant engineers design combustion processes within the limitation of the flammable range of the fuel. Flammable fuel/ air compositions generate high temperatures ( $> 1600^\circ\text{C}$ ) and produce  $\text{NO}_x$  by the nitrogen fixation reaction (reverse of reaction (1)). Catalytic systems do not require that the fuel/air mixture be flammable to initiate oxidation, consequently reaction can be initiated with a leaner mixture with adiabatic temperatures below that required for the  $\text{NO}_x$  formation reaction. Furthermore, the combustion is so efficient that  $\text{CO}$  and  $\text{HC}$  emissions are less than 2 ppm.

Modern gas turbine power plants require turbine inlet temperatures between  $1300$  and  $1350^\circ\text{C}$ . These temperatures can be met by catalytic combustion but issues related to durability of the catalyst and monolithic substrate remain to be demonstrated on large scale systems<sup>1</sup>. This breakthrough technology represents a quantum leap in clean and efficient combustion technology for the 21st century.



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## DIRECT CATALYTIC RECOVERY OF ELEMENTAL SULFUR FROM SULFUR DIOXIDE- LADEN STREAMS

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## ABSTRACT

Single-stage catalytic reduction of  $\text{SO}_2$  to elemental sulfur is a promising new technology better suited to treat  $\text{SO}_2$ -laden streams generated in power plants and certain industries than the conventional multi-stage Claus process. It is anticipated that a simple, single-stage sulfur recovery process will decrease the cost and accelerate the commercialization of advanced technologies, such as gasification combined-cycle power plants employing regenerative gas desulfurization. Recovery of the sulfur value from  $\text{SO}_2$ -Containing off-gas in elemental form is also environmentally sound; thus, sulfur is an innocuous, low-volume, and potentially saleable byproduct. The reduction of  $\text{SO}_2$  to elemental sulfur over catalysts comprising transition metal promoted fluorite-type oxides, such as cerium oxide, are discussed in this presentation. These new catalysts have high activity and selectivity to elemental sulfur over a wide range of operating conditions. Reductants include carbon monoxide, syngas and natural gas at temperatures in the range of  $450^\circ\text{C}$  (for syngas) to  $700^\circ\text{C}$  (for methane). The catalyst properties are illustrated here by the system of copper or nickel oxide in cerium oxide or doped cerium oxide. Results from parametric and structural studies are presented.

## INTRODUCTION

More than 170 wet scrubber systems applied to 72,000 MW of U.S. coal-fired, utility boilers are in operation or under construction<sup>1</sup>. A small fraction (of the order 1 percent<sup>2</sup>) of these systems produce a usable byproduct (gypsum): the remainder generate approximately 20 million tons per annum of disposable flue gas desulfurization (FGD) byproduct, which are transported and disposed of in landfills<sup>3</sup>. The use of regenerable sorbent technologies has the potential to reduce or eliminate this solid waste production, transportation and disposal.

All regenerable FGD systems produce an off-gas stream from the regenerator that must be processed further in order to obtain a saleable byproduct, such as elemental sulfur, sulfuric acid or liquid  $\text{SO}_2$ . This off-gas has only a fraction of the flue gas volume, and contains no oxygen. Recovery of elemental sulfur from this stream in a single-stage catalytic converter, avoiding a multi-stage Claus plant, could decrease the cost and accelerate the commercialization of many regenerable FGD processes. Even when there is no market for the sulfur, elemental sulfur constitutes only one-third of the volume of the equivalent  $\text{CaSO}_4$  byproduct, and is completely innocuous. Therefore, no secondary pollution issues ensue from this approach.

A single-stage catalytic process for the conversion of  $\text{SO}_2$  to sulfur is under development at Lawrence Berkeley Laboratory using mixed metal oxide catalysts<sup>4</sup>. Sulfur yields as high as 98% have been reported at  $500^\circ\text{C}$  with dry or wet syngas as the reductant at atmospheric pressure and low space velocity (2100 v/v/h). Another process under development is the Direct Sulfur Recovery Process (DSRP) at the Research Triangle Institute<sup>5</sup>. This reports high sulfur yields at  $627^\circ\text{C}$  at relatively low space velocity (3750 v/v/h) and high pressure (21.4 atm).

In recent work, we have found that cerium oxide undoped or doped with rare earth oxides is a highly active and stable catalyst for  $\text{SO}_2$  reduction by  $\text{CO}$ <sup>6-8</sup>. Doped cerium oxide is a fluorite-type oxide, well known for its high oxygen storage capacity. This refractory material keeps its crystal structure in the highly reactive sulfur

atmosphere. The catalyst activity and resistance to impurities, such as water vapor, of the fluorite oxide catalysts can be significantly enhanced by addition of small amounts of transition metals, such as Cu, Ni, Co, etc<sup>6,7</sup>. The CeO<sub>2</sub>-based catalysts can be used for the reduction of dilute as well as concentrated SO<sub>2</sub>-streams. The team Tufts University, Arthur D. Little and Engelhard Corporation is conducting Phase 1 of a four and a half , two-phase effort to develop and scale-up an advanced sulfur recovery technology that is based on a direct, single-stage, catalytic reduction of sulfur dioxide to elemental sulfur over the new metal modified ceria catalysts<sup>9</sup>. In this paper we discuss the salient features of SO<sub>2</sub> reduction by CO, syngas and methane over the transition metal/fluorite-type oxide catalysts, focusing on the reactivity of copper or nickel-modified cerium oxide for illustration.

## SUMMARY

Catalysts were prepared by the urea gelation/coprecipitation method using metal nitrate precursors<sup>9</sup>. After air calcination at 650°C for 12 h, the typical surface area of the CeO<sub>2</sub>-based catalysts was in the range of 70-120m<sup>2</sup>/g. Urea-precipitated CeO<sub>2</sub> had smaller crystal size (10.5 nm) than CeO<sub>2</sub> prepared by acetate decomposition (20 nm). Doping with 10% La or Zr stabilizes the crystal size of ceria and improves its resistance to sintering, and increases its reducibility (oxygen storage capacity). The reduction behavior depends on the ceria surface area (surface oxygen reduction) and also on oxygen ion conductivity (bulk reaction). Both the surface and bulk reduction of ceria can be modified by doping.

The microcrystallinity, defect formation and reducibility of ceria are all important factors for its activity in redox reactions<sup>10</sup>. Indeed, the SO<sub>2</sub> reduction by CO, which has been reported as a redox reaction<sup>11</sup>, shows a clear correlation of activity with the above properties of doped ceria. Thus, the most active catalyst was Ce (10% Zr)O<sub>2</sub> with 50% SO<sub>2</sub> conversion at 380°C, and 90% conversion at 410°C in a gas mixture containing (in mol) 1% SO<sub>2</sub>, 2% CO, 97% He and at a contact time of 0.09 g•s/cm<sup>3</sup>(S.V. = 80,000 v/v/h).

Transition metal oxides, while immiscible with ceria, can increase its reducibility through strong interfacial interaction. Thus, a small amount of a transition metal can be added to ceria to improve its activity especially in wet gas streams<sup>6-8</sup>. Furthermore, the addition of transition metals can modify the selectivity of the doped ceria to elemental sulfur product. The presence of copper in Ce(La)O<sub>2</sub> improves the water-gas-shift activity of the latter. Thus, in wet gas streams containing CO and SO<sub>2</sub>, formation of byproduct H<sub>2</sub>S is observed as a result of the reaction of H<sub>2</sub> with surface sulfur. On the other hand, the choice of nickel as a metal modifier of ceria can give different product yields since the Ni-Ce(La)O<sub>2</sub> is not as active a catalyst as Cu-Ce(La)O<sub>2</sub> for the water-gas-shift reaction.

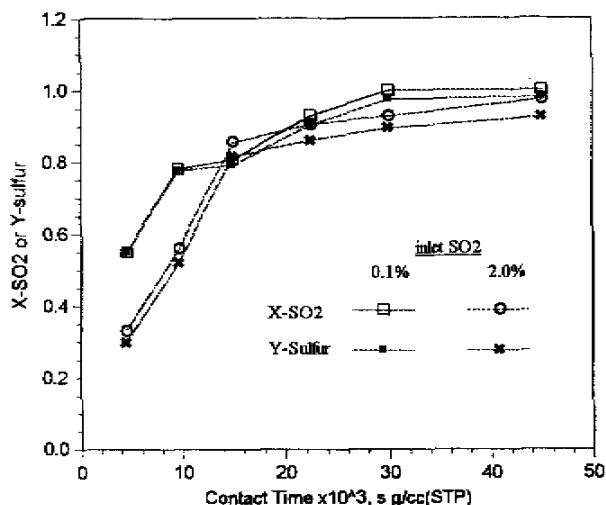
Transition metal oxides themselves are active catalysts for SO<sub>2</sub> reduction by CO or syngas. However, transition metals are typically sulfided under reaction conditions. A reaction mechanism involving COS intermediate has been proposed for such catalysts<sup>11</sup>. Elemental sulfur is produced by the reduction of SO<sub>2</sub> by COS. According to this mechanism high COS levels would be observed at short contact times. In extensive parametric studies of the new metal-modified ceria catalysts including fixed-bed microreactor and TGA-mass spectrometry tests, we have not detected COS as a reaction intermediate. Thus, elemental sulfur is a primary product over these catalysts. COS (or H<sub>2</sub>S) is a secondary product formed by reaction of excess CO (or H<sub>2</sub>) with the produced sulfur. Hence, short contact times, i.e. high space velocities, can be used with the new catalysts without any reduction of sulfur yield.

Figure 1 shows plots of typical kinetics obtained in microreactor with powders of the Cu<sub>0.15</sub>[Ce(La)]<sub>0.85</sub>O<sub>x</sub> catalyst containing 15 at% Cu and 4.5 at% La. In these tests the SO<sub>2</sub> concentration was varied from 0.1 to 2%, while keeping the molar ratio of CO to SO<sub>2</sub>, R<sub>CO</sub>, close to 2. The contact time was controlled by changing both the catalyst loading and flow rate. In this figure, X-SO<sub>2</sub> is the conversion of SO<sub>2</sub>, defined as  $X\text{-SO}_2 = ([\text{SO}_2]_{\text{in}} - [\text{SO}_2]_{\text{out}})/[\text{SO}_2]_{\text{in}}$ ; Y-sulfur is the yield of elemental sulfur, defined as  $Y\text{-sulfur} = [\text{sulfur}]_{\text{out}}/[\text{SO}_2]_{\text{in}}$ . The  $[\text{sulfur}]_{\text{out}}$  is calculated from the difference of  $[\text{SO}_2]_{\text{in}} - [\text{SO}_2]_{\text{out}} - [\text{H}_2\text{S}]_{\text{out}} - [\text{COS}]_{\text{out}}$ , based on gas chromatography of the exit gas stream (using a 1/4" O.D. by 6' long Chromosil 310-packed column and a thermal conductivity detector). With all inlet SO<sub>2</sub> concentrations and contact times tested, elemental sulfur was the dominant product. The catalyst was so active that more than 30% SO<sub>2</sub> conversion was obtained at 510°C at the very short contact time of 0.0045 g•s/cm<sup>3</sup> (STP), which corresponds to a space velocity of about 1,000,000 v/v/h.

The catalytic performance of transition metal/fluorite oxide composite catalysts is explained by the redox reaction mechanism<sup>8,11</sup>. A synergistic catalyst model was derived from comprehensive kinetics and structural studies of the Cu-Ce(La)O<sub>x</sub> model catalyst. Reaction takes place over surface oxygen vacancy sites which are created by

reduction of surface oxygen with CO. In the Cu-Ce(La)O<sub>x</sub> system, the stable cerium oxide serves as the backbone of the catalyst structure and as the oxygen source, while copper promotes the reducibility of the cerium oxide and provides surface sites for CO adsorption. SO<sub>2</sub> has strong affinity to cerium oxide, such that a working Cu-Ce(La)O<sub>x</sub> catalyst comprises both partially reduced and partially sulfated cerium oxide<sup>8,11</sup>.

The activity of Cu-Ce(La)O<sub>x</sub> catalysts for SO<sub>2</sub> reduction by synthesis gas (H<sub>2</sub> + CO) is similar to that for SO<sub>2</sub> reduction by CO. However, the presence of H<sub>2</sub> promotes the production of H<sub>2</sub>S and lowers the sulfur yield. This is more pronounced with Ni-modified ceria catalysts. Single-staged operation with both high SO<sub>2</sub> conversion and high sulfur yield is possible with coal-derived syngas (H<sub>2</sub>/CO=0.3-1) on both types of catalysts. Proper choice of catalyst composition and operating conditions will be required when H<sub>2</sub>-rich synthesis gas is used as reductant of SO<sub>2</sub>.



**Figure 1.** Variation of SO<sub>2</sub> conversion and sulfur yield over Cu<sub>0.15</sub>[Ce(La)]<sub>0.85</sub>O<sub>x</sub> catalyst with contact time at T=510 °C (R<sub>CO</sub>=2).

Reduction of SO<sub>2</sub> by methane, which is the main component of natural gas, can also take place over the microcrystalline CeO<sub>2</sub> and La- or Zr-doped ceria catalysts. Methane activation is hard to achieve over a partially sulfated surface and light-off temperatures are typically about 200°C higher than for the reduction of SO<sub>2</sub> by syngas. Ni- and Cu-modified ceria catalysts with low metal content (~2 wt%) are active for this reaction. A 70% sulfur yield was obtained over the Ni<sub>0.04</sub>[Ce(La)]<sub>0.96</sub>O<sub>x</sub> catalyst at 700°C and a space velocity of ca. 15,000 v/v/h with a stoichiometric mixture of SO<sub>2</sub> and CH<sub>4</sub>. Water had a minor inhibition effect on the catalyst activity. The present studies indicate that the catalyst activity and sulfur yield can be further improved by optimizing the catalyst formulation, surface area and process conditions.

In summary, the Ni-Ce(La)O<sub>x</sub> and Cu-Ce(La)O<sub>x</sub> oxide composites of low transition metal content have been identified as promising new catalysts for application to a single-stage, highly efficient catalytic converter of SO<sub>2</sub> to elemental sulfur with a variety of industrial reducing gas streams.

## ACKNOWLEDGMENTS

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**HETEROGENEOUS CATALYTIC HYDROGENATION OF CHLOROFLUOROCARBONS**

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**ABSTRACT**

Hydrodechlorination is an important technology for the manufacture of hydrofluorocarbons and recycle of chlorocarbons and chlorofluorocarbons. Yet, the catalytic chemistry of these ubiquitous compounds is poorly understood. This project started as a collaboration between Industry, University and Government to understand this chemistry. We were able to determine kinetic parameters and are making progress in understanding the reaction mechanism. The combination of unique expertise in the university, equipment in the national laboratory and practical knowledge in industry were key factors in the success of this project. The current understanding of hydrodechlorination chemistry and the areas of research that need attention will be presented. It is also illustrated how computational chemistry can help in understanding the catalytic chemistry.

**INTRODUCTION**

Chlorofluorocarbons have numerous applications in current technologies but they are undesirable nowadays because these compounds are perceived as harmful to the environment. To replace these compounds, hydrofluorocarbons with similar properties are used. Until a technology for the controlled addition of fluorine to hydrocarbons is developed, the production of hydrofluorocarbons will invariably require the synthesis of an intermediate chlorofluorocarbon followed by hydrodechlorination.

Examples of hydrogenation of chlorofluorocarbons are in the synthesis of new refrigerants<sup>1</sup> and the synthesis of monomers to produce Teflon-like materials<sup>2</sup>. Another application that is very important nowadays is the transformation of byproduct organic molecules containing chlorine into valuable feedstock<sup>3</sup>. Despite these and other important applications of hydrodechlorination, basic knowledge of the catalytic chemistry of the reaction is lacking. For example, rates for the reaction of hydrodechlorination cannot be easily found. One reason is that there are many possible analogues of the molecule under study and they may show completely different rates. There is a drastic dependence of rate to the environment of the halogen atoms in the molecule but no theory to help correlate rate with structure. Only if the same molecule has been studied before on the same catalyst can rates be compared. Even then, the lack of knowledge on the kinetics makes the reported rates difficult to compare.

To be able to quickly advance knowledge in this area, a collaboration was started among national laboratory (LBNL), industry (DuPont), and university (UCB) and it took advantage of the unique expertise in each place. The national laboratory and university in this case provided the unique experimental equipment and technical approach not available otherwise and industry provided the operational knowledge of the system and guidance to interpret the results. As stressed in the Vision 2020 document, this is indeed a very effective combination for acquiring knowledge.

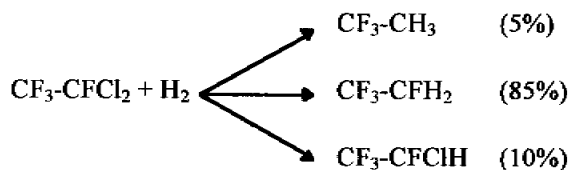
We will describe briefly the state of knowledge of hydrodechlorination as exemplified in the case of CFC 114a ( $\text{CF}_3\text{-CFCl}_2$ ) and a Pd catalyst. The areas of research that need attention will also be discussed.

**OVERVIEW OF HYDRODECHLORINATION**

The hydrodechlorination of chlorinated organic molecules have received much less attention from the research community than, for example, hydrocarbon chemistry. The reason may be the much bigger economical importance of hydrocarbons. However, it has been realized now that the ubiquitous chlorinated organic molecules can have an adverse effect on the environment and it has become economically important to understand this chemistry. There have been reports on the catalytic chemistry of hydrodechlorination but we will not discuss them here for lack of space. Instead, we will point at some key results that are missing. For example,

what is the relationship between the structure of the catalyst and rates and selectivity and can rates be predicted based on the rates of a similar compound?

We will present our preliminary answer to these questions through the study of hydrodechlorination of CFC 114a ( $\text{CF}_3\text{-CFCl}_2$ )<sup>4</sup>. This molecule can be used in the production of HFC 134a ( $\text{CF}_3\text{-CFH}_2$ ), an ozone-friendly reffigerant. The reaction network over Pd is:

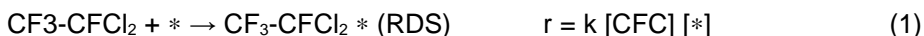


(scheme 1)

We found out that the rate of the three reactions above are independent of the structure of the catalyst. The turnover rates are all the same on Pd(100), Pd(111), Pd foil and a 0.5% Pd supported on carbon, catalysts with widely different structures. These experiments were performed in a specially designed apparatus where model catalysts can be prepared and characterized under ultrahigh vacuum conditions and then transferred to a reactor for the measurement of reaction rates at the same conditions as industrial catalysts. The insensitivity to the structure is a very significant finding for practical and fundamental reasons. It indicates that the rate will be proportional to the total Pd area on the catalyst and thus a Pd catalyst will always show the same rate and selectivity regardless of its origin. It is tempting at this point to conclude that hydrodechlorination reactions over Pd are all insensitive to the structure of the catalyst. Is it the same true for other metals? That remains to be shown.

We also found that the reaction selectivity is independent of conversion, which implies that the reactions in scheme 1 above occur in parallel on the catalyst surface. To investigate further the reaction mechanism the reaction order dependence was determined<sup>4</sup>.

Based on these kinetic parameters, the following reaction mechanism is proposed for the two main products HCFC 124 ( $\text{CF}_3\text{-CFCIH}$ ) and HFC 134a ( $\text{CF}_3\text{-CFH}_2$ ). The rate determining step is the non-dissociative adsorption of the reactant CFC 114a:



(Other steps for the CFC hydrodechlorination are not kinetically significant)

It is also assumed that Cl is the most abundant reaction intermediate

$$[*] + [\text{Cl}*] = [\text{L}] \quad (2)$$

where [L] is the total number of sites, and that the surface is equilibrated with  $\text{H}_2$  and HCl in the gas phase:



The number of free sites can then be calculated from (2) and (5) and it is equal to  $[*] = K [\text{H}_2]^{0.5}/[\text{HCl}]$ . The final rate will then be

$$r = k K [\text{CFC}] [\text{H}_2]^{0.5}/[\text{HCl}] \quad (6)$$

which is a good approximation to the experimentally observed rate dependencies for HCFC 124 and HFC 134a.

The rate dependence on HFC 143a ( $\text{CF}_3\text{-CH}_3$ ) does not fit the above mechanism. The above mechanism implies that the almost zero order dependence on  $\text{H}_2$  should also correspond to a zero order dependence on HCl. Further data are necessary to investigate this matter.

Another important finding is the -1 reaction order dependence in HCl. This finding implies that the rates are a function of conversion and it thus should always be reported. There are many unresolved questions on this chemistry. We are still not able to predict rates for different compounds and the reaction mechanism is

incomplete for this reaction. In particular, the reaction selectivity for the reaction above cannot be explained. To help us understand this chemistry we are making use of theoretical methods to guide our experiments. The strategy is to collaborate closely with an expert on quantum mechanical calculations (M. Neurock, Univ. Virginia) to help us decide if a proposed mechanism is feasible. This method of approaching catalytic problems with a combination of experimental and theoretical methods will be the way to solve problems efficiently in the future. Initial results from first-principle Density Functional Theoretical (DFT) methods indicate that  $\text{CF}_3\text{CFCl}_2$  binds to Pd(111) through very weak van der Waal interactions (20 kJ/mol) between the two chlorine atoms and two surface palladium atoms. In light of the interaction, it appears likely that the chemistry may proceed through two sequential Pd-atom insertion steps into the C-Cl bonds to create the  $\text{CF}_3\text{-CF}^*$  surface intermediate.

The  $\text{CF}_3\text{-CF}^*$  intermediate binds most strongly through the uncoordinated  $\text{CF}^*$  carbon atom sitting at a Pd-Pd bridge site with a surface binding energy of 385 kJ/mol. This is more stable than the  $\text{CF}_3\text{-CCl}^*$  analogue which binds at the same site with only 343 kJ/mol. We are currently examining the explicit potential energy surfaces for C-Cl and CF bond activation chemistry over palladium. The mechanisms are likely to be similar to those already found for C-H activation of substituted ethyl surface species. Computational results for adsorption, C-X activation and desorption steps on a series of model surfaces will be used to compare against measured surface kinetics.

Another problem with these catalysts is the long term deactivation. it may be caused by interaction of fluorine with the support, which in turn weakens the metal-support interaction causing the metal to move and to agglomerate. This problem will be approached by studying the carbon support by UV laser Raman spectroscopy.

## SUMMARY

The reaction of hydrodechlorination of CFC 114a over Pd is structure insensitive. The reaction mechanism involves the non-dissociative adsorption of CFC 114a as the rate determining step. The HCl generated in the reaction inhibits the reaction and thus the conversion level must be reported together with the rates. Many questions still remain to be answered in this chemistry. The approach used in this research was a combination of efforts from Industry, University and Government and it was very effective. We are pursuing the current research with quantum mechanical modeling of the reactions to gain insight on the catalytic chemistry.

## ACKNOWLEDGMENTS

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## ON THE INVENTION OF CHEMICAL REACTIONS FOR ATOM ECONOMY

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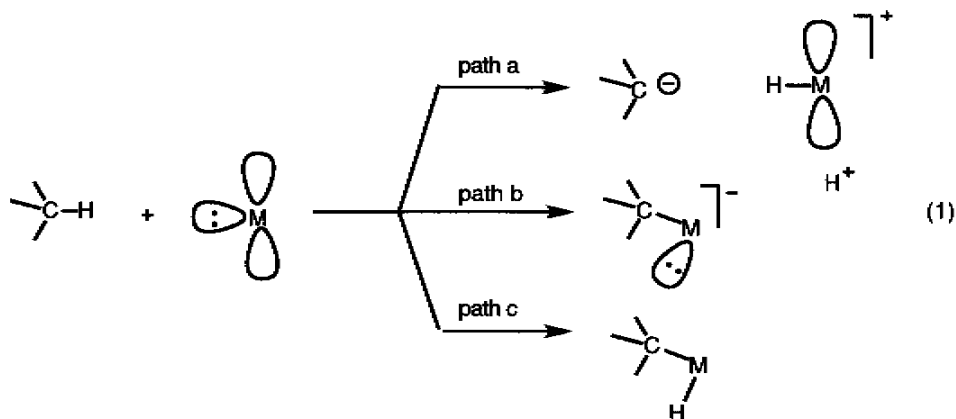
The ever increasing sophistication of the molecular entities to perform a myriad of functions from materials science to biology creates great needs for innovative synthetic methodology to convert simple, readily available building blocks to the targets. Enhancing efficiency has largely focused upon issues of selectivity. To minimize the number of synthetic steps, reactions must be able to discriminate among different bonds, even some of the same type, i.e., must be chemoselective. Minimization of production of isomeric by-products requires a number of different kinds of selectivity. Orienting two reaction partners avoids generating regioisomers. Controlling relative stereochemistry minimizes production of undesired diastereomers. Many molecules have the capability of existing in a pair of spatial relationships which relate them to each other by a mirror plane. Normally, it is desirable to synthesize only one of these isomers or enantiomers.

In the zeal to address the issues of selectivity, a second fact of synthetic efficiency is frequently overlooked. In a very simple sense, it considers the question of how much of what you put into your pot ends up in your product. Use of raw materials with maximal efficiency and minimal production of by-products and waste are the motivators for asking this question. Such a question is so fundamental to the commodity chemical industry that it has been a major consideration in the development of new improved processes. However, the specialty chemical industry (including pharmaceuticals and agrichemicals) which undoubtedly will be playing an increasingly important role in the U.S. economy has not traditionally placed emphasis on such issues. Many factors require a rethinking of such issues even in the very high valued end product segment of the specialty chemical industry.

A fundamental part of this task is the development of chemical reactions which utilizes 100% of the starting materials to produce 100% of the product with no by-product or waste production and anything else being required only catalytically. Thus, an ideal reaction is an addition in which every atom of the starting materials ends up in the product—i.e., the reaction is atom economic.<sup>1,2</sup> While such reactions do exist, they are relatively few. If our repertoire of addition reactions increased significantly, then the prospects to enhance atom economy in a synthetic scheme will increase significantly.

This lecture considers such a task in the context of invention of new additions catalyzed by transition metal complexes. An initial concept considers one of the fundamental concepts in chemistry—Bronsted acids and bases. A low valent metal fits the definition of a Bronsted acid (eq. 1, path a). In this scenario, it may remove a proton from a carbon acid to generate a carbon centered nucleophile and a "metal hydride" electrophile.

Alternatively, it also fits the definition of a Bronsted base (eq. 1, path b). Here, a transition metal organometallic is created. Finally, a low valent metal may undergo an "oxidative addition" to generate an organometallic wherein both the carbon and hydrogen is bound to the metal (eq. 1, path c). Each of these scenarios offers opportunities for invention and are discussed.



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**IMPLICATIONS OF THE GREEN CHEMISTRY MOVEMENT TO ACADEMIA  
AND THE ENVIRONMENTAL SCIENCE COMMUNITY**

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The rise of the Green Chemistry movement, and more generally, the evolution of industrial ecology as the new paradigm for environmental protection and energy conservation, raises fundamental questions about the role of academic institutions in the research process and in the training of the next generation of environmental professionals. Intellectual property rights are only one of the relevant issues. In addition, the environmental science community will increasingly be occupied with impacts of new processes and new products as opposed to remediation efforts. The scope of this research will be global, interdisciplinary and increasingly complex, forcing environmental scientists to develop more accurate predictive tools. This presentation will explore these and other aspects of the industrial ecology movement.

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**ENVIRONMENTALLY CONSCIOUS CHEMICAL PROCESSING AT THE NATIONAL SCIENCE FOUNDATION**

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The NSF has often played a leadership role in identifying and stimulating research in both cutting edge science and in promising new technologies. The pattern is clear in the original presentation of a program, "Environmentally Benign Chemical Synthesis and Processing" by the Chemical and Transport Systems Division of the NSF with participation by the Chemistry Division as well. This paper will review the definition of that program and the character of its early awards. The idea of pollution prevention as opposed to waste treatment is now conventional wisdom.

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# BIOSYNTHESIS



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## **BIOCATALYTIC ALTERNATIVES TO CURRENTLY-EMPLOYED CHEMICAL SYNTHESSES AND PRODUCTS**

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Fundamental environmental improvement can be accomplished by replacing environmentally-problematic synthesis of a given chemical with an environmentally-benign chemical synthesis. Alternatively, a chemical product synthesized by an environmentally-problematic synthesis can be replaced with a chemical synthesized via an environmentally-benign route. Examples of both approaches to source reduction of pollutants will be illustrated with the use of microbial biocatalysis and renewable feedstocks. Biocatalytic and currently-employed syntheses will be compared based on their compatibility with a sustainable economy, use of toxic starting materials/intermediates, and generation of environment-damaging byproducts. Since any "green" alternative must be competitive with the manufacturing costs of currently-employed chemical syntheses and products, titer and yield considerations during microbial biocatalysis will be discussed.

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## **CONVERSION OF WASTE BIOMASS TO ANIMAL FEED, CHEMICALS, AND FUELS**

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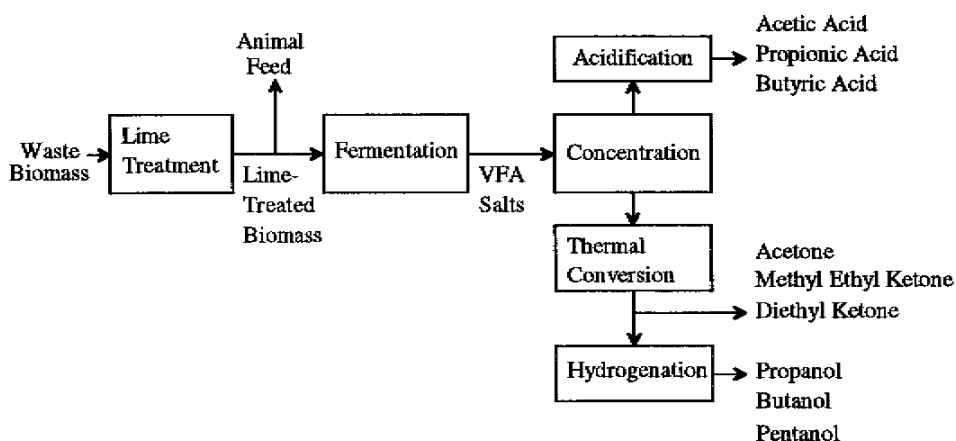
### **ABSTRACT**

Waste biomass includes municipal solid waste (MSW), municipal sewage sludge (SS), industrial biosludge, manure, and agricultural residues. When treated with lime, biomass is highly digestible by a mixed culture of acid-forming microorganisms. Lime treatment doubles the ruminant digestibility of agricultural residues; thus, it may be used to upgrade their feed value. Alternatively, lime-treated biomass can be fed to an industrial-scale mixed-acid fermentation where acetic, propionic, and butyric acids are produced. To control the pH, these acids are neutralized with calcium carbonate. The resulting calcium salts may be thermally converted to ketones - such as acetone, methyl ethyl ketone, and diethyl ketone - which are useful industrial solvents. Further, these ketones may be hydrogenated to alcohols - such as propanol, butanol, and pentanol - which may be used as industrial solvents or motor fuel. Alternatively, the calcium salts may be acidified to recover the acids. In recognition of the potential environmental benefits of this technology, it has been awarded the 1996 Presidential Green Chemistry Challenge Award.

### **INTRODUCTION**

Waste biomass resources are underutilized; in fact, many have a cost associated with their disposal. At Texas A&M, we have developed a family of technologies that converts waste biomass into animal feed, industrial chemicals and fuels (see Figure 1). In the first step, the waste biomass is treated with lime to render it more digestible. Lime-treated agricultural residues (e.g. straw, stover, bagasse) may be used as ruminant animal feeds. Alternatively, the lime-treated biomass can be fed to a large anaerobic fermentor in which rumen microorganisms convert the biomass into volatile fatty acid (VFA) salts such as calcium acetate, propionate, and butyrate. The VFA salts are concentrated and may be converted into chemicals or fuels via three routes. In one route, the VFA salts are acidified releasing the acetic, propionic, and butyric acids. In a second route, the VFA salts are thermally converted to ketones such as acetone, methyl ethyl ketone, and diethyl ketone. In a third route, the ketones may be hydrogenated to their corresponding alcohols such as propanol, butanol, and pentanol.

These technologies offer many benefits for human health and the environment. Lime-treated animal feed can displace feed grains, thereby reducing soil erosion and use of fertilizers, herbicides, and pesticides that can contaminate ground water.



**Figure 1.** Process schematic.

Chemicals (e.g. organic acids and ketones) may be economically produced from waste biomass that has a negative impact on the environment, such as MSW and SS. Typically, these wastes are landfilled or incinerated which incurs a disposal cost while causing land or air pollution. By producing chemicals from waste biomass, nonrenewable resources such as petroleum and natural gas, are conserved for later generations. Because 50% of U.S. petroleum consumption is now imported, displacing foreign oil will help reduce the U.S. trade deficit.

Fuels (e.g. alcohols) produced from waste biomass have the benefits cited above, i.e., reduced environmental impact from waste disposal and reduced trade deficit. In addition, oxygenated fuels derived from biomass are clean burning and do not add net carbon dioxide to the environment, thereby reducing global warming.

### TECHNOLOGY OVERVIEW

Figure 1 shows a schematic of our technologies for converting waste biomass into animal feed, chemicals and fuels. Regardless of the final product, the waste biomass first is treated with lime to render it more digestible. Table 1 shows that lime treatment essentially doubles the ruminant digestibility of agricultural residues.

**Table 1.** Ruminant Digestibility of Untreated and Lime-Treated Agricultural Residues

Agricultural Residue	48-h Digestion	
	Untreated	Lime Treated
Sugar-cane bagasse	30.8%	62.7%
African millet straw	45.1%	89.9%
Sorghum straw	54.1%	82.9%
Tobacco stalks	34.4%	67.9%
Treatment: 0.1 kg Ca(OH)/kg dry biomass, 9 kg H <sub>2</sub> O/kg dry biomass, 2 h, 100°C.		

We can exploit this mixed culture of rumen microorganisms to convert waste biomass into VFA's that, in turn, may be converted to useful chemicals and fuels. This approach contrasts the traditional approach in which waste biomass is enzymatically hydrolyzed to sugars that are subsequently fermented to products via a pure culture of microorganisms. Our approach has the following advantages:

- The system is adaptable to a wide variety of feedstocks because a mixed culture of microorganisms converts the biomass to VFA salts.
- Sterile process conditions are not required.
- Inexpensive tanks can be employed.
- Expensive extracellular enzymes are not required because the microbes make their own enzymes.
- The fermenting organisms do not have to be purchased because they regenerate themselves.
- Cells and enzymes can be recycled without contamination risk.
- The fermenting organisms are stable.
- The process is robust so specially skilled operators are not required.
- There are no viable contaminants to the process, so spoiled batches do not have to be disposed of.

In the fermentor, to prevent the pH from dropping too low, the VFA's produced by the mixed culture of

microorganisms are neutralized with limestone; therefore VFA salts (e.g. calcium acetate, propionate, and butyrate) are the fermentation product. These salts are concentrated using a proprietary energy-efficient, capital-efficient process.

The concentrated VFA salts may be easily converted to one of two products: VFA's or ketones. VFA's are produced through a proprietary process in which the acidifying agent is recycled; thus, no wastes are produced. Ketones are produced by thermal conversion of the VFA salts. At 430°C, the reaction is complete in just a few minutes. The ketones may be subsequently hydrogenated to alcohols. Using 50-g/L Raney nickel catalyst, the hydrogenation is complete in less than 1 h. Regardless of the final product, the calcium salts are recycled back through the process so that no wastes are generated.

## ECONOMICS

We have performed some preliminary economic evaluations of our chemical and fuel technologies. The following scenarios were considered:

**Scenario 1:** Using very conservative assumptions, it is possible to expect incomes of about \$60/dry tonne for accepting waste materials in the Northeast. Using this scenario, the selling price of the products is shown in Table 2 using a 45% return on investment (ROI).

**Scenario 2:** To use the process in more regions of the country, less ROI and less income must be received for accepting the waste. Table 2 shows the selling price assuming the biomass can be obtained for free and that a 15% ROI is acceptable.

**Scenario 3:** Large quantities of agricultural residues are available in the U.S. and tropical countries. Bagasse is a prime candidate because it is already collected. It is valued at about \$20/tonne for its energy content. Table 2 shows the selling price assuming agricultural residues can be obtained for \$20/tonne and a 15% ROI is acceptable.

In all scenarios, the selling prices are favorable compared to current chemical prices. The mixed alcohols are inexpensive enough that they can compete with the fuel oxygenates methyl tertiary butyl ether (MTBE) and ethanol which are valued at about \$0.80/gal and \$1.10/gal, respectively.

**Table 2.** Selling Price of Fuels and Chemicals

Product	Scenario 1	Scenario 2	Scenario 3	Price
Mixed Alcohols	\$0.59/gal	\$0.72/gal	\$0.88/gal	\$1.70/gal isopropanol
Mixed Ketones	\$0.53/gal	\$0.68/gal	\$0.84/gal	\$2.52/gal acetone \$2.96/gal methyl ethyl ketone
Mixed Acids	\$0.052/lb	\$0.060/lb	\$0.073/lb	\$0.33/lb acetic acid \$0.44/lb propionic acid \$0.48Ab butyric acid
Scenario 1: 45% ROI and -\$60/dry tonne biomass Scenario 2: 15% ROI and \$0/dry tonne biomass Scenario 3: 15% ROI and \$20/dry tonne, biomass				

## SUMMARY

At Texas A&M, we are developing a family of technologies that converts waste biomass to animal feeds, chemicals, and fuels. By displacing grains used to feed animals, we will reduce soil erosion and water contamination with fertilizers, herbicides, and pesticides. Biomass-derived chemicals and fuels are completely renewable and reduce our dependence on imported oil. Biomass-derived fuels are clean-burning, high-octane oxygenates that do not contribute net carbon dioxide to our atmosphere thereby mitigating global warming. By using waste biomass as a feedstock in our process, rather than disposing of it by landfilling or incineration, we eliminate both economic and environmental costs associated with its disposal.

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**TANDEM ENZYME-ASSISTED AND ELECTROCHEMICAL METHODS OF SYNTHESIS:  
TOWARD A REAGENT-FREE APPROACH TO CHEMICAL MANUFACTURING**

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Aromatic dioxygenases are relied on for the conversion of halogenated aromatic compounds to optically pure diene diol metabolites. These synthons are manipulated further in brief synthetic sequences to valuable end-products in the carbohydrate and alkaloid realm. Several new reaction conditions for oxidative and reductive manipulations of these synthons have recently been developed by relying on electrochemical methods rather than on traditional and sometime toxic reagents. Recent progress in the syntheses of several biologically important targets will be presented with the focus on effective technology for pollution prevention in manufacturing of fine chemicals and intermediates important in the pharmaceutical industry.



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# **PROCESS & REACTOR DESIGN**



## LOW VOC ALKYD COATING RESINS BY MINIEMULSION COPOLYMERIZATION

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### ABSTRACT

Alkyd resins are commonly used in oil-based architectural finishes. In an effort to develop a water-borne alkyd coating resin, grafting to acrylic copolymers was carried out by emulsion and miniemulsion copolymerization of acrylic monomers in the presence of an alkyd resin. The results demonstrate that miniemulsion polymerization is the preferred process, probably because of mass transport limitation of the alkyd in the conventional emulsion polymerization reaction. Reaction rate, particle size, grafting efficiency, and degree of crosslinking were measured. Liquid films of the emulsions were prepared on wood substrates using a Baker draw down blade. The dried films demonstrated good clarity, hardness and adhesion properties. It is expected that this techniques will combine the best qualities of alkyd resins with water borne acrylic emulsions to produce interior/exterior latex coatings.

### INTRODUCTION

Water-based coatings, have become more widely used in the past several decades because they are environmentally friendly, they offer easier clean up and, their properties and application performance characteristics have improved. Solvent based systems such as alkyd resins have remained important for some applications because of superior properties such as gloss and hardness. This work examines the feasibility of polymerizing acrylic monomers in the presence of alkyd resins to determine if this hybrid system offers the advantages of alkyd coatings (specifically durability) in a water-based coating. The polymerizations were carried out in both emulsion and miniemulsion polymerization systems.

Emulsion and miniemulsion polymerizations have many similarities, but particle nucleation and reagent transplant phenomena are very different. Conventional emulsion polymerization is started with a monomer emulsion comprised of relatively large (in the range of 5-10 microns) monomer droplets and significant free or micellar surfactant.

Particle nucleation takes place early in the reaction via homogeneous (water phase) polymerization followed by precipitation, or via free radical entry into monomer-swollen micelles. Radicals can enter the monomer droplets, but this phenomenon is generally discounted because of the relatively small droplet surface area. Nucleation stops or slows significantly after the surface area of the particles becomes sufficient to adsorb all of the surfactant from the micelles. The major locus of polymerization thereafter is in the nucleated particles. The monomer must move from the monomer droplets to the reaction sites in the particles by diffusion.

Miniemulsion polymerization, by contrast, begins with submicron monomer droplets. High intensity fluid deformation and a hydrophobe (or cosurfactant) are employed to generate and stabilize the small droplet size miniemulsion. No micelles are present since excess surfactant has been adsorbed onto the large droplet-water interfacial area. Particle nucleation is primarily via droplet penetration and, the monomers or comonomers are located at the site of polymerization sites and mass transport, except for the radicals, is not involved.

If it is desired to graft an alkyd resin into an acrylic polymer, the alkyd must be at the site of the reaction. Since most alkyds of interest are quite water-insoluble, emulsion polymerization may not give good grafting efficiency, since alkyd transport from the monomer droplets to the polymer particles may be limited. Miniemulsion polymerization, on the other hand, does not require transport of the alkyd across the aqueous phase, and so should result in higher grafting efficiencies.

### EXPERIMENTAL

Miniemulsion and macroemulsion polymers were produced from the recipes shown in Table 1. The miniemulsions were prepared by dispersing the desired amount of monomer-PMMA-alkyd solution (some additional runs contained 0.5 wt % BPO) in the aqueous SLS solution by mixing with a rotating stirrer at room temperature. The resulting emulsion was sheared further by sonication with a Heat Systems 474 W Sonicator Ultrasonic Processor XL for 10 minutes at 21% output (100 W).

The monomer miniemulsion was polymerized at 60 or 80 °C. The emulsion polymerizations were carried out in the same manner except that no sonication was used and the PMMA hydrophobe was not employed.

**Table 1.** Recipe for Emulsion and Miniemulsion Polymerizations

<u>Sample Code</u>	<u>Ingredients (wt %)</u>				
	<u>MMA</u>	<u>PMMA</u>	<u>BA</u>	<u>AA</u>	<u>Alkyd</u>
EA00	49	0.0	50	1.0	0.0
EA05	49	0.0	50	1.0	5.0
EA100	49	0.0	50	1.0	100.0
MA00	45	4.0	50	1.0	0.0
MA30	45	4.0	50	1.0	30.0
MA60	45	4.0	50	1.0	60.0
MA100	45	4.0	50	1.0	100.0

1. The continuous phase consists of 250 parts water per 100 parts total monomer, 0.02 mmol/L water sodium lauryl sulfate, and 0.02 mmol/L water potassium persulfate.
2. The alkyd resin percentage is based on the total monomer weight.
3. EA are emulsion polymerizations. MA are miniemulsion polymerizations.

## RESULTS AND DISCUSSION

The monomer miniemulsions with PMMA as hydrophobe, were prepared with different amounts of alkyd resin. The PMMA hydrophobe was shown to be effective in the preparation of kinetically stable miniemulsions. The alkyd-acrylate miniemulsions were much more stable than normal emulsions prepared without PMMA. Their shelf lives varied from 7 hours to more than 50 days. The size of monomer droplets was below 300 nm. The polymerization rate with alkyd was slower than that without alkyd. Doubling the initiator and surfactant concentration increased the reaction rate, but not to the level achieved with the miniemulsion polymerization without alkyd. The low reaction rates in the presence of alkyd may be caused by a retarding impurity in the alkyd or by resin chain transfer that produces an inactive radical. Low reactivity when emulsion polymerizing vinyl acetate and styrene in the presence of alkyd was noted by Cummings<sup>3</sup>. To circumvent this problem, he used a mixed initiator (water and oil soluble components) in much the same way as was done here. The latexes obtained from the miniemulsion polymerization of the alkyd-acrylate mixtures, were uniform emulsions, and no coagulation was observed.

The alkyd used in these experiments is made from linseed and soya fatty acid and polyols<sup>4</sup>. The double bonds in the alkyd can react with free radicals, but the alkyd double bonds will have a different reactivity than the vinyl bonds in acrylate monomers. It is desired to know if grafting and/or crosslinking occur, and to what extent. The alkyd-acrylate polymers and blends of pure alkyd and pure MMA-BA-AA copolymer were analyzed by <sup>13</sup>C-NMR for residual double bond content. The results show that only 20 to 30% of the double bonds in the alkyd react. This confirms that the alkyd is copolymerized with the acrylates and that the final polymer product is an alkyd-acrylate copolymer not an alkyd-polyacrylate blend. Approximately 70 to 80% of the double bonds in the alkyd remains in the alkyd-acrylate latex after reaction, which could enhance curing as the latex is dried during application. The grafting ratio was tested by extraction. Approximately 70% of the polyacrylate was grafted onto alkyd in Run MA100 which contained equal amounts of monomers and alkyd. Crosslinking was investigated by exhaustive extraction of the alkyd-acrylate copolymer. Less than 5.24% crosslinked or highly branched copolymer.

In order to obtain preliminary information on potential application performance, films were formed from five products on wood and metal substrates. These films were made from latex product directly from the reactor with 1% (wt/wt latex) hydroxy ethyl cellulose as a thickener, using a Baker Coater draw-down, and dried at room temperature. ASTM Hardnesses were all "B" which is acceptable for common coatings. These results, considering that there has been no formula optimization or compounding, are encouraging.

## SUMMARY AND CONCLUSIONS

The miniemulsion polymerization process has proved to be effective for incorporating an alkyd resin into acrylic coating copolymers. The reaction produces stable, small particle size latexes which contain graft copolymer of the acrylic and alkyd components. This technique may be useful for obtaining some of the desirable properties of solvent-based alkyds in a solvent-free aqueous latex form.

The support of the National Science Foundation in the form of Grants CTS-9224813 and CTS-9417306 and to the Environmental Protection Agency for Grant R825326 is gratefully acknowledged.

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## POLLUTION PREVENTION THROUGH MASS INTEGRATION

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## ABSTRACT

This paper provides an overview of recent advances in the field of pollution prevention via mass integration. First, the key strategies for reducing industrial waste are discussed. Then process integration is presented as a viable tool for systematizing pollution prevention decisions. Three key elements of process integration are discussed: synthesis, analysis and optimization. Systematic techniques for developing mass integration strategies are illustrated. These strategies include segregation, mixing, recycle, interception and sink/generator manipulation. Case studies are used to demonstrate the uniqueness and effectiveness of this novel methodology.

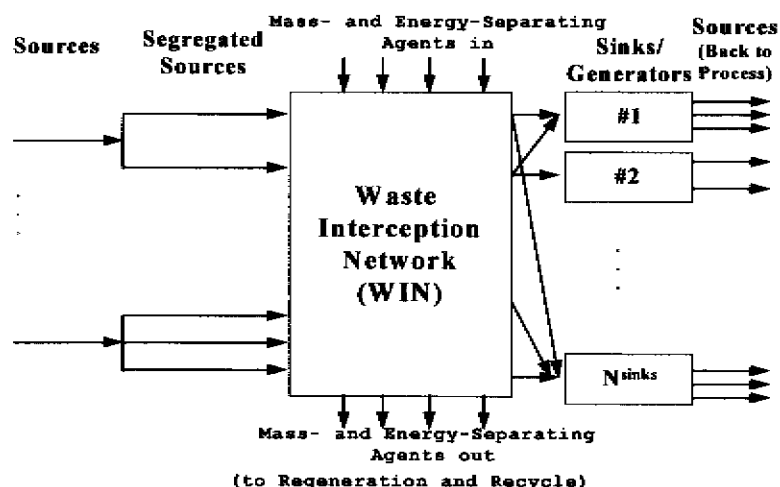
## INTRODUCTION

A chemical process is an integrated system of interconnected units and streams, and it should be treated as such. Process integration is a holistic approach to process design, retrofitting, and operation which emphasizes the unity of the process. Two key branches of process integration have been developed: **mass integration and energy integration**. **Mass integration** is a systematic methodology that provides a fundamental understanding of the global flow of mass within the process and employs this understanding in identifying performance targets and optimizing the generation and routing of species throughout the process. Mass-allocation objectives such as pollution prevention are at the heart of mass integration. Mass integration is more general and more involved than energy integration. Mass integration provides a systematic framework for understanding the big picture of the process, identifying performance targets, and developing solutions for improving process efficiency including pollution prevention.

## MASS INTEGRATION STRATEGIES

Mass integration is based on fundamental principles of chemical engineering combined with system analysis using graphical and optimization-based tools. The first step in conducting mass integration is the development of a global mass allocation representation of the whole process from a **species viewpoint** (El-Halwagi et al., 1996; El-Halwagi and Spriggs, 1996) as shown in Fig. 1. For each targeted species (e.g., each pollutant), there are sources (streams that carry the species) and process sinks (units that can accept the species). Process sinks include reactors, heaters/coolers, biotreatment facilities, and discharge media. Streams leaving the sinks become, in turn, sources. Therefore, sinks are also generators of the targeted species. Each sink/generator may be manipulated via design and/or operating changes to affect the flowrate and composition of what each sink/generator accepts and discharges.

In general, sources must be prepared for the sinks through segregation and separation via a waste-interception network (WIN) (El-Halwagi et al, 1996). Effective pollution prevention can be achieved by a combination of stream segregation, mixing, interception, recycle (with or without interception) and sink/generator manipulation. The following sections summarize these concepts.



Segregation simply refers to avoiding the mixing of streams. In many cases, segregating waste streams at the source renders several streams environmentally acceptable and hence reduces the pollution-prevention cost. Furthermore, segregating streams with different compositions avoids unnecessary dilution of streams. This reduces the cost of removing the pollutant from the more concentrated streams. It may also provide composition levels that allow the streams to be recycled directly to process units.

**Figure 1.** Schematic representation of mass-integration strategies for pollution prevention.

Recycle refers to the utilization of a pollutant-laden stream (a source) in a process unit (a sink). Each sink has a number of constraints on the characteristics (e.g. flowrate and composition) of feed that it can process. If a source satisfies these constraints it may be directly recycled to or reused in the sink. However, if the source violates these constraints segregation, mixing, and/or interception may be used to prepare the stream for recycle.

Interception denotes the utilization of separation unit operations to adjust the composition of the pollutant-laden streams to make them acceptable for sinks. These separations may be induced by the use of mass-separating agents (MSAs) and/or energy separating agents (ESAs). A systematic technique is needed to screen the multitude of separating agents and separation technologies to find the optimal separation system. The synthesis of MSA-induced physical-separation systems is referred to as the synthesis of mass-exchange networks (MENs) (El-Halwagi and Manousiouthakis, 1989). Interception networks using reactive MSAs are termed reactive mass exchange networks (Srinivas and El-Halwagi, 1994; El-Halwagi and Srinivas, 1992). Network synthesis techniques have also been devised for other separation systems that can be used in intercepting pollutants. These systems include pressure-driven membrane separations (e.g., El-Halwagi, 1992), heat-induced separation networks (HISENs) (e.g., Dunn et al., 1995; Dye et al., 1995; Richburg and El-Halwagi, 1995; El-Halwagi et al., 1995) and distillation (e.g., Malone and Doherty, 1995; Wahnschafft et al., 1991).

Sink/generator manipulation: involves design or operating changes that alter the flowrate or composition of pollutant-laden streams. These measures include temperature/pressure changes, unit replacement, catalyst alteration, feedstock substitution, reaction-path changes (e.g., Crabtree and El-Halwagi, 1995), reaction system modification, and solvent substitution.

Extensive discussion on mass integration techniques and environmental case studies has been recently compiled in a textbook (El-Halwagi, 1997).

## SUMMARY

Mass integration is a systematic framework for addressing pollution prevention problems along with other process objectives. It provides insights that smoothly guide the engineer through process complexities and steer the designer towards cost-effective solutions. Notwithstanding its relatively recent development, over the past ten years mass integration has been successfully applied to more than twenty industrial projects. Typically, the solutions generated by mass integration are intuitively non-obvious and are significantly superior to non-integrated solutions.

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## INTELLIGENT SYSTEM FOR COMPREHENSIVE WASTE MINIMIZATION IN ELECTROPLATING PLANTS

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Electroplating plants are major waste generators in the manufacturing industries. The quantity and toxicity of the waste streams must be significantly reduced. Waste minimization (WM) in plating lines has become one of the main tasks for the metal finishing industries in the next decade.

A PC based intelligent decision support system, namely IDS-P2EP, is developed for WM in electroplating plants. It contains a variety of first principles-based process models which characterize the dynamic behavior of all major unit operations. With these models, precise information on waste generation can be obtained, comprehensive and pertinent WM strategies can be made for a plating plant of any size and any type. The system can provide engineers the opportunities of analyzing environmental problems, gaining new insights, consulting pre-solved example problems, or otherwise deriving alternative solutions. The applications of this system in a plating plant strongly demonstrate that it can greatly help them significantly reduce a variety of pollutants in waste streams with the lowest cost.





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# DESIGN OF MATERIALS



## ASSESSING THE LIFE CYCLE ENVIRONMENTAL IMPACTS OF MATERIALS: A CASE STUDY COMPARING ALTERNATIVE ELECTRIC VEHICLE BATTERIES

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### ABSTRACT

A variety of analysis frameworks for characterizing the life cycle environmental impacts of materials have emerged over the past 5-10 years. This preprint briefly reviews those frameworks and illustrates their strengths and weaknesses using a high profile case study assessing the environmental impacts of batteries that could be used in electric vehicles. The analysis compares lead-acid, nickel-cadmium, nickel-metal hydride, and sodium-sulfur batteries. Quantitative and qualitative data on the environmental performance of these alternative batteries were assembled and evaluated. No clear environmental winner could be selected from the four battery designs chosen for the study, but the analysis reveals data gaps, areas for environmental improvement and key design issues that determine the environmental performance of the batteries.

### INTRODUCTION

Environmental labeling programs, and environmentally driven procurement programs are some of the many initiatives that are increasing interest in methods for assessing the environmental impacts of materials. While many methods have emerged for assessing the environmental impacts of materials, there are no universally accepted methodologies. Even the metrics that are to be used in deciding whether a material is "green" are fiercely debated. There are, however, a few common elements in the most widely accepted methodologies for evaluating the environmental impacts of materials. Among these are:

- Assessment frameworks should take a life cycle perspective, considering all environmental impacts from the initial extraction of raw materials, through manufacturing and consumer use, to eventual product reuse, recycling or disposal;
- Multiple environmental impact categories should be considered. While there is no consensus about what set of environmental impacts should be considered, it is generally accepted that single criteria are not appropriate.

Thus, the information needed to complete a typical environmental assessment of a material can be summarized in a matrix, with the life cycle stages along the columns and impact categories making up the rows. This methodology has been described by Graedel, et al. (1995). The strengths and weaknesses of the approach are best illustrated through case studies. This preprint briefly describes a case study which compared the materials used in four competing electric vehicle battery systems. A more complete description of this case is available elsewhere (Steele, 1995; Steele and Allen, 1997).

### ELECTRIC VEHICLE BATTERIES

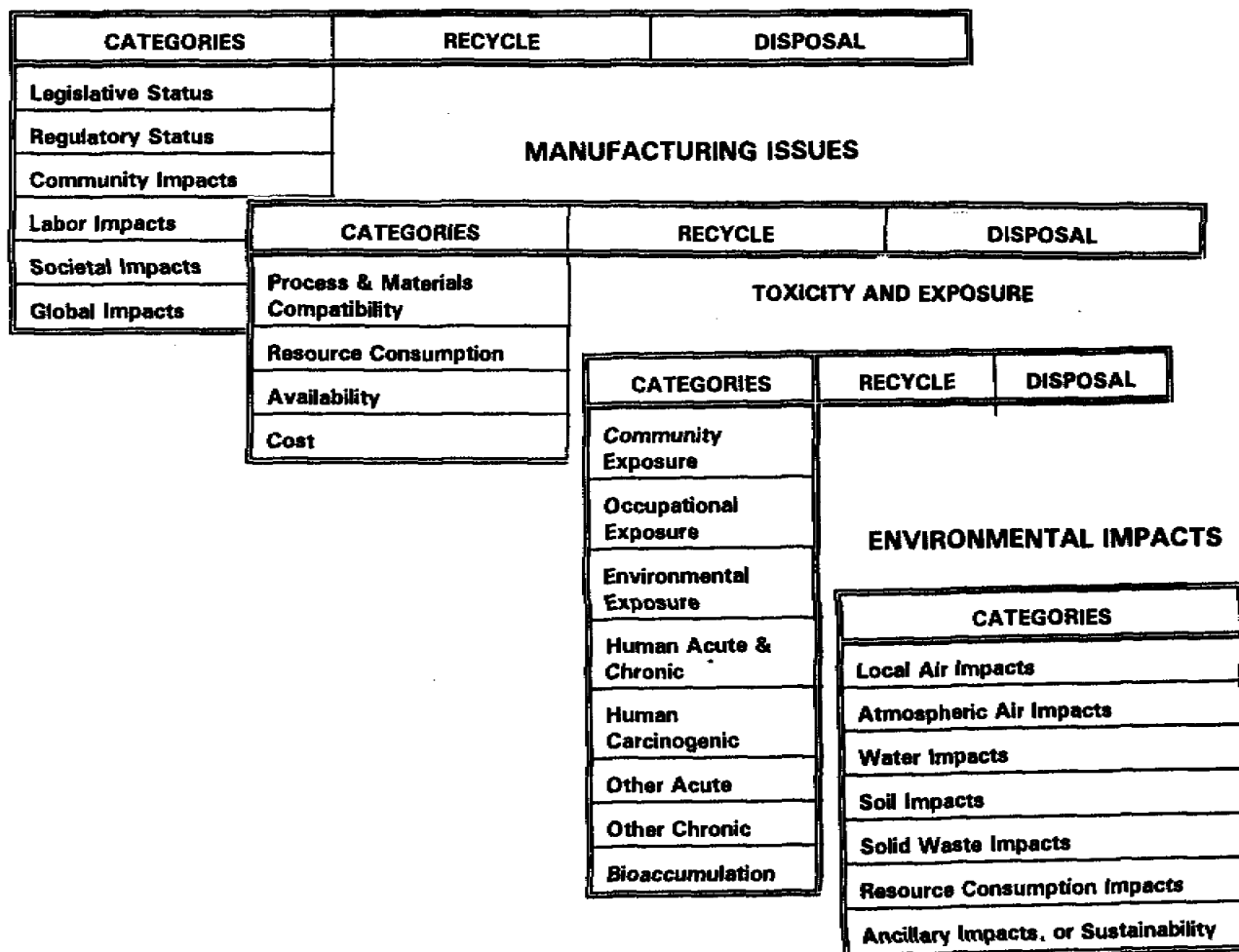
The four battery systems chosen for this comparison were those deemed most likely to be used in electric vehicles (EVs) in the next ten years (CARB, 1993). Batteries now used in EVs are lead-acid, nickel-cadmium, nickel-iron and sodium-sulfur. Nickel-metal hydride batteries are often considered mid-term batteries. Each of these technologies, with the exception of nickel-iron, was considered in this analysis. Each battery was evaluated in a semi-quantitative manner using the matrices shown in Figure 1. The matrices include impacts to the ambient environment, impacts due to toxicity and human exposure, social and regulatory variables and manufacturing issues. These impact categories were evaluated for recycling and disposal operations. This end of product life focus was chosen because it is anticipated that in the long term, most electric vehicle batteries will be recycled, as is the current practice for automotive batteries. If approximately 95% of electric vehicle batteries are recycled, then the contribution of the recycling life cycle stage will be critically important in assessing environmental impacts of batteries. Disposal practices were included to recognize the lack of a recycling infrastructure for many battery types. Until recycling infrastructures develop, disposal will be important for some batteries.

Each matrix element was evaluated for each battery type by assigning a score, ranging from 0 to 5, with a high score representing a significant impact. The evaluation was based on a review of quantitative data. As an example of the procedure, consider the human carcinogenicity data for recycling lead acid batteries. This matrix

element was evaluated by examining risk assessments done for recycling facilities in California. The risk assessments were done in response to the California Air Toxics Hot Spots law (AB 2588) and estimated that *lifetime risk* was 16 extra cancer cases per million people, due primarily to emissions of arsenic, cadmium, and nickel. This matrix element was assigned a score of 5, representing a moderate to severe negative impact. Some of the assessments had considerable uncertainty. One type of uncertainty arose from conflicting sources of data. The most glaring example of this type of uncertainty is the matrix element for the local air impacts associated with recycling of lead acid batteries. Lead emissions were the primary concern in evaluating this matrix element. Rates of emission of lead from recycling operations were estimated using emission factors, data from the Toxic Release Inventory normalized by battery throughput, data from the California Air Resources Board and the results of an Electric Power Research Institute study. The estimates of lead emissions per 1000 kg of Pb recovered are listed in Table 1. The estimates vary over approximately 3 orders of magnitude. While this is an extreme example of data variability, it does dramatically illustrate the high degree of uncertainty associated with measuring flows of metals in recycling operations. Another type of uncertainty is due to a complete lack of data. For example, only bench scale recycling of Na-S batteries has been performed and most nickel reprocessing is done for non-automotive batteries. A partial listing of the overall results is given in Figure 2. Space limitations prevent us from showing all of the impact categories for all of the batteries. These are available elsewhere (Steele, 1995; Steele and Allen, 1997).

### SUMMARY

No clear environmental leader emerges from among the battery types. This is typical of comparisons between materials. Each material has a profile of environmental impacts that are difficult to compare. Nevertheless, qualitative environmental impact assessments, such as the case study summarized in this preprint, are useful in identifying data gaps, key areas for environmental improvements and design issues that determine environmental performance.

**SOCIAL AND POLITICAL VIABILITY****Figure 1.** Impact Assessment Matrices Used to Evaluate Electric Vehicle Batteries**REFERENCES**

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**Table 1.** Emissions data for Secondary Lead Smelters as Reported by Different Sources

Data Source	Releases of Pb to the atmosphere (metric tons per facility)	Emission Factor (kg Pb emissions per 1000 kg Pb produced)
U.S. EPA <sup>9</sup>		7.3
U.S. EPA 1987 TRI		1.8
1992 TRI data (facility #1)	5.05	0.034
1992 TRI data (facility #2)	2.16	0.0087
EPRI Study <sup>10</sup>		0.00775
California Air Resources Board	0.7-1.7	

**Figure 2.** Environmental Impact Assessment Matrices Used to Evaluate Electric Vehicle Batteries (The matrix elements indicate approximate environmental impact where 0 is negligible and 5 is significant; the uncertainty level (low, medium or high) is also characterized)

CATEGORIES	NICKLE METAL-HYDRIDE		SODIUM-SULFUR	
	RECYCLE	DISPOSAL	RECYCLE	DISPOSAL
Local Air Impacts	4 high	3 medium	4 low	4 low
Atmospheric Air Impacts	3 low	3 low	3 low	3 low
Water Impacts	4 high	4 high	3 medium	3 medium
Soil Impacts	4 medium	3 low	3 low	3 low
Solid Waste Impacts	4 medium	5 medium	5 medium	5 medium
Resource Consumption Impacts	4 low	4 low	4 low	4 low
Ancillary Impacts, or Sustainability	2 low	5 low	2 low	5 low

CATEGORIES	LEAD-ACID		NICKEL-CADMIUM	
	RECYCLE	DISPOSAL	RECYCLE	DISPOSAL
Local Air Impacts	5 low	3 low	5 medium	3 low
Atmospheric Air Impacts	4 medium	3 low	3 medium	3 low
Water Impacts	4 medium	3 low	4 medium	3 low
Soil Impacts	5 low	3 low	5 medium	3 low
Solid Waste Impacts	4 low	5 medium	4 medium	5 medium
Resource Consumption Impacts	4 low	4 low	4 low	4 low
Ancillary Impacts, or Sustainability	2 low	5 low	2 low	5 low

## BIOBASED RESINS FOR COMPUTER COMPONENTS AND PRINTED WIRING BOARDS

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### ABSTRACT

Lignin, a by-product of paper manufacturing, has been used to develop a new series of resins for various computer components, particularly printed wiring boards (PWB). PWB's are commonly fabricated from epoxy/fiberglass laminates onto which electrical components are mounted. Replacement of the current petroleum derived phenolic epoxy resins with bio-based materials would reduce the environmental concerns with the fabrication, assembly, and disposal of PWB's. Resins used in PWB's must have a high glass transition temperature, low moisture absorption, high thermal stability, flame retardancy and good dielectric properties. Lignin is the only common phenolic-based biopolymer, thus it is naturally hydrophobic and has good thermal stability. Resin formulations which are lignin/epoxy blends (containing at least 50% lignin) exhibit acceptable physical and electrical properties for a wide range of applications, including PWB's. Laminates formed from lignin

based resins can be processed in a similar fashion to current laminates, minimizing the financial considerations of converting to this resin system.

## INTRODUCTION

Thermosetting epoxy resins are used in a variety of applications in computer and electronics assembly and manufacturing. Specifically, epoxies are used as chip encapsulants and underfills to reduce stress on solder joints, as molding compounds for non-hermetic chip enclosures, and in fiberglass reinforced laminates for printed wiring boards. Printed wiring boards probably account for the largest volume use of epoxy resins.

Printed wiring boards are found in a wide range of products, including computers, VCR's, cameras, and automobiles. The demand for PWB's is increasing rapidly - the world market for PWB's has increased at an average rate of two billion dollars/year since 1983 to a current value of approximately \$25 billion. It is estimated that 27 million square meters of laminate was used in manufacturing the PWB's that were produced domestically in 1993<sup>1</sup>, consuming approximately 24 million kilograms of epoxy resin. Of increasing concern is the disposal of the more than 150 million square meters of laminate that are produced globally each year. The majority of PWB's are disposed of via incineration to reclaim the precious metals content, with a lesser amount sent to hazardous waste landfills (due to lead based solders used to attach electrical components)<sup>2</sup>. Incineration of any petroleum based materials increases the CO<sub>2</sub> level in the atmosphere, contributing to the potential "greenhouse effect" which may lead to global warming and other detrimental environmental changes. Incineration of materials generated from biobased sources returns CO<sub>2</sub> to the atmosphere that was already part of the existing CO<sub>2</sub> cycle (similar to the effects of biodegradation of that same material in nature). There is mounting evidence that the incorporation of biobased materials, including lignin, may actually increase the rate of biodegradation of synthetic components to which they are bound<sup>3</sup>. While it is obvious that changes in any single industry may not dramatically alter these environmental balances, it is essential that every industry takes additional responsibility for its individual contributions before significant improvements will be achieved.

The use of renewable resources as raw materials have additional environmental advantages. Natural products, especially if used in a form similar to that in which they occur in nature, generally take less energy to produce than their petroleum-based counterparts<sup>4</sup>. Effluent (solid, liquid, or gaseous) reductions may also be possible by choosing an appropriate biobased raw material. Lignin, for example, is produced as a by-product of the paper manufacturing industry, but it has few industrial uses. Very little additional energy or processing are required to isolate it in a form that may be usable as a primary raw material for resin manufacture.

Conversion of any portion of the computer industry to biopolymer based resin systems would require resins that are compatible with current manufacturing technology and pricing structures. PWB's and other packaging applications in the computer industry are essentially mature technologies with low profit margins. Introduction of new materials, even if they offer environmental benefits, will require an equivalent, if not improved profit margin to gain wide acceptance. The profit margin is reflected in both the pricing structure of the raw materials as well as the processing and fabrication costs. Ideally, any new environmentally based resins would be transparent in processing requirements.

To be applicable for printed circuit board fabrication, a bio-based resin must meet all current PVM requirements for performance and reliability. Most biopolymers are composed of linear or cyclic aliphatic organic chains (e.g. proteins and polysaccharides) with a high density of polar functional groups. Such polymers have unacceptable properties for electrical laminates due to their low thermal stability, low dimensional stability, and high moisture absorption. The only phenolic biopolymer is lignin. Lignin occurs naturally in the cell walls of plants as a highly branched polymer that constitutes up to 33% of the dry weight of wood. Lignin is naturally hydrophobic and has high thermal stability. Numerous studies have reported success in incorporating lignin into phenolic or epoxy based resins<sup>5</sup>. The use of lignin in PWB's would reduce the environmental and disposal concerns associated with the current PVM technology and replace non-renewable oil based resins with a renewable resource that is currently considered to be a waste product.

## EXPERIMENTAL

### A. Materials.

Lignins from several sources were evaluated. Lignin derived from the Kraft (alkaline based) pulping process was obtained from Westvaco, Inc. (Charleston Heights, SC). Lignin derived from the Organosolv (aqueous/alcohol based) pulping process was obtained from Repap, Inc. of Canada. Lignin derived from a steam explosion pulping process was obtained from Stake Technologies. Various brominated and non-brominated diglycidyl ethers of

bisphenol A were obtained from Shell Chemical Co. and Ciba Geigy Corp. Polyfunctional epoxy novolacs were obtained from Dow Chemicals and Ciba Geigy Corp. Arme initiators were obtained from Aldrich Chemical Company. All chemicals except the Kraft and steam exploded lignins; were used as received. The Kraft and steam exploded lignins were washed repeatedly in water and dilute acidic solutions to remove inorganic salts left over from the alkaline pulping or isolation processes,

### *B. Experimental Techniques.*

Pure resin samples were prepared by dissolving all of the components of the resin in a small quantity of solvent (alcohol/ketone mixtures). The solvent was removed under vacuum prior to curing. Resin samples were cured at 150°C for two hours. Thermal analyses (DSC, TMA, and TGA) were performed on TA Instruments Models 2910, 2940, and 2950. Prepreg was prepared by applying the resin solutions to various styles of glass cloth on laboratory, pilot scale and manufacturing prepreg towers. Lamination was performed using standard FR4 lamination conditions (e.g. 150-190°C, 300-600 psi for 30-120 min.). Laminate testing was performed both at IBM's testing facilities in Endicott, NY and at Trace Labs, Hunt Valley, MD using standard test procedures for FR4 laminate evaluation.

### **SUMMARY**

To be accepted by the printed wiring board industry, a bio-based laminate resin must meet all of the current materials specifications for epoxy laminate resins at no increase in materials or tooling costs. Under this set of constraints, the options to chemically modify lignin were eliminated. Our resin formulations have focused on unmodified lignin. As there is no viable non-enzymatic method for self-condensation of lignin, resins were formulated using a co-reactant. Epoxide/phenol reactions are commonly used in laminate resin formulations, and a similar system was employed here for lignin resins. Formulations of lignin with di- or poly-functional phenol based epoxies employing an appropriate amine catalyst were evaluated and will be discussed.

Samples of laminate were evaluated for a variety of physical and electrical properties alongside FR4 controls. The results of these evaluations are presented in Table IV. In essentially all cases the properties of the lignin/epoxy laminate meet or exceed the standard IPC requirements for FR-4 laminate. Physical properties such as glass transition temperature, coefficient of thermal expansion, decomposition temperature, and moisture absorption indicate that the lignin/epoxy resin performs very favorably compared to the FR4 controls.. The electrical performance of lignin/epoxy resin samples also exceeds a of the IPC requirements for FR4 laminate, and the measured permittivity value of 3.98 at 1 MHz is essentially equivalent to that of FR4 produced in the same facility. Laminates of this lignin/epoxy prepreg have been used to build test vehicles with up to eight layers of copper wiring using standard PWB manufacturing chemicals and processing protocols. The lignin laminate was compatible With all of the current processing techniques. The test vehicles are presently under evaluation for performance, reliability and cost effectiveness.

### **ACKNOWLEDGMENT**

We would like to acknowledge the contributions of Bob Japp and Bill Fotorny for overseeing the production scale prepreg manufacture, John Surowka and Gerry Kohut for laminate testing, Jeff Hedrick and Nancy LaBianca for assistance in lab scale prepreg fabrication, and Gareth Hougham for dielectric measurements on the pure resins. This work was partially funded by ARPA under the Environmentally Conscious Electronics Manufacturing Initiative, contract number F33615-95-C-5509.

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**TABLE IV.** Materials Properties of Lignin Resin Laminates

	IPC Standards for FR4	Lignin Laminate	FR4 Control
Glass Transition Temperature (°C)	>110	140	128
Coefficient of Thermal Expansion (µm/m°C)			
Below Tg	X	17.2	24.2
	Y	27	24.2
	Z	67	606
Above Tg	X	6.8	14.6
	Y	7.8	11.3
	Z	372	430
Decomposition Temperature (°C)		314	313
Moisture Absorption, max. (wt%)			
24 Hour Room Temperature Water	0.8	0.32	0.35
16 Hour Boiling Water		1.76	2.18
1 Hour Pressure Cooker		1.27	1.72
Flexural Strength (Kpsi) - lengthwise	60	[82]	
- crosswise	50	[58]	
Copper Peel Strength of 1 oz. Copper Foil (lb/in)	6	7.3	
Permittivity, max (at 1 MHz)	5.4	4	4
Dissipation Factor, max. (at 1 MHz)	0.035	0.021	0.015
Volume Resistivity, min. (Mohm-cm)	40	[>45]	
Surface Resistivity, min. (Mohm-cm)	10 <sup>6</sup>	[10 <sup>8</sup> ]	
Dielectric Breakdown, min. (kV)	10 <sup>4</sup>	[10 <sup>8</sup> ]	
Electrical Strength, min. (sec.)	750	[900]	
Arc Resistance, min. (see.)	>60	[66]	
Flammability	UL V-0	UL V-0	UL V-0

[ ] Tested by Trace Laboratories, all other testing at IBM Endicott

#### NEXT GENERATION ENHANCEMENT OF CEMENTS BY THE ADDITION OF INDUSTRIAL WASTES AND SUBSEQUENT TREATMENT WITH SUPERCRITICAL CO<sub>2</sub>

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#### ABSTRACT

The natural curing reactions which occur in a standard portland cement involve the formation of portlandite, Ca(OH)<sub>2</sub>, and calcium silicate hydrates, CSH. Over time, the cured cement abstracts carbon dioxide, CO<sub>2</sub>, from

the air, converting the portlandite and CSH to calcium carbonate,  $\text{CaCO}_3$ . It turns out, however, that this secondary conversion results in the blockage and/or closure of pores, impeding the ingress of reactants ( $\text{CO}_2$ ) and the egress of reaction products ( $\text{H}_2\text{O}$ ), drastically slowing the reaction rate with time. It is known that even extremely old cements, such as that in the dome of the Parthenon in Greece, are still undergoing this natural carbonation reaction! By exposing a portland cement to supercritical  $\text{CO}_2$  (SCCO<sub>2</sub>), it is found that the carbonation reaction can be greatly accelerated. This acceleration is due to (1) the ability of the supercritical fluid to penetrate into the pores of the cement, providing continuous availability of fresh reactant, in hyper-stoichiometric concentrations; and (2) the solubility of the reaction product in the supercritical fluid, facilitating its removal. By accelerating the natural aging reactions, a chemically stable product is formed having reduced porosity, permeability and pH, while at the same time significantly enhancing the mechanical strength. The supercritical  $\text{CO}_2$  treatment process also removes a majority of the hydrogenous material from the cement, and sequesters large amounts of carbon dioxide, permanently removing it from the environment.

We will describe the general features of supercritical fluids, as well as the application of these fluids to the treatment of cements containing industrial waste. Some of the issues concerning the economic feasibility of industrial scale-up will be addressed. Finally, some initial results of physical property measurements made on portland cements before and after supercritical fluid  $\text{CO}_2$  treatment will be presented.

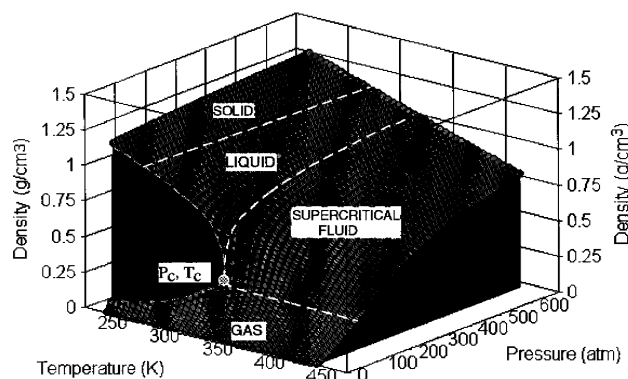
## INTRODUCTION

To illustrate the concept of a supercritical fluid, let us examine the situation of a quantity of liquid in a closed container, subjected to slow, uniform heating. As the container is heated, the density of the liquid decreases because of normal thermal expansion. Simultaneously, the density of the vapor increases as more molecules leave the liquid and enter the gas phase. If the heating continues, a temperature will be reached, called the critical temperature ( $T_c$ ), where the density of the liquid is so reduced, and that of the vapor phase is so increased, that the density of the two phases become equal. When this occurs, then since the density and temperature inside the container is everywhere equal, the pressure is everywhere equal. This is the critical pressure,  $P_c$ . A liquid that has been brought to conditions above  $T_c$  **and**  $P_c$  is defined as a supercritical fluid (SCF).

A comparison is given in Table 1 of selected physical properties of the liquid, gas and SCF states of a typical organic substance. The gas-like properties of low viscosity and high diffusivity of supercritical fluids provides for effective mass transport into granular and micro-porous matrices, while the high, liquid-like density provides for a relatively good solvating power. Figure 1 shows the pressure-temperature-density surface for pure  $\text{CO}_2$ . It can be seen that relatively small changes in temperature or pressure, above the critical values  $T_c$  and  $P_c$ , can result in large changes in density. It is this tunability of density which is one of the most attractive features of supercritical fluids, since the fluid solubility can often be made selective for a specific solute within a solute mixture. Finally, since there is no longer a phase boundary between the liquid and gas phases, there are no surface tension forces to overcome. This provides for excellent, substrate independent wetting.

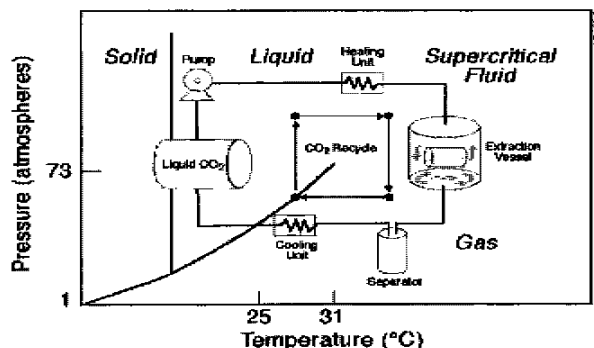
**Table 1.** Comparison of physical properties of a typical organic fluid in the liquid, gas, and supercritical fluid state.

	Diffusivity ( $\text{cm}^2/\text{s}$ )	Viscosity ( $\text{g}/\text{m}\cdot\text{s}$ )	Density ( $\text{g}/\text{cm}^3$ )
liquid	$10^{-5}$	1	1
supercritical fluid	$10^{-3}$	$10^{-1}$	0.3
gas	$10^{-1}$	$10^{-2}$	$10^{-3}$



**Figure 1.** Pressure-temperature-density surface of pure  $\text{CO}_2$ .

Figure 2 shows a schematic pressure-temperature phase diagram for CO<sub>2</sub>, which also incorporates a process flow diagram for a closed-loop extraction system. The SuperScrub™, which is part of the Supercritical Fluids Facility at the Los Alamos National Laboratory, is a fully-automated, closed-loop system, with a 60-liter-capacity extraction vessel which can operate at pressures up to 5000 psi and temperatures up to 60°C. The maximum flow rate is 500 pounds of CO<sub>2</sub> per hour. We are currently using this system to optimize the treatment conditions which give the best combination of cement properties, as well as to develop the engineering methodology necessary for scale-up to an industrial process.



**Figure 2.** Pressure-temperature phase diagram of pure CO<sub>2</sub> with a superimposed flow diagram for a closed-loop, supercritical-fluid extraction process.

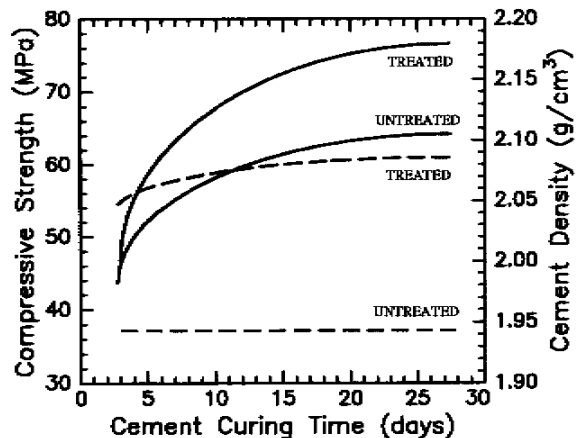
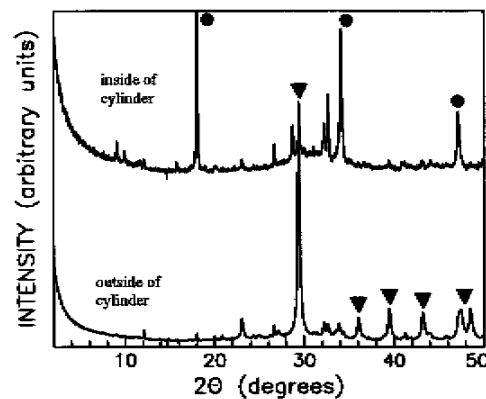
Supercritical CO<sub>2</sub> is an excellent choice for large-scale extraction processes for several reasons. CO<sub>2</sub> is non-toxic, non-flammable, and inexpensive (10 - 40 cents per pound). Its critical conditions of temperature and pressure, 31°C and 1072 psi, are easily achievable in existing process equipment. There is already a transportation and distribution infrastructure (virtually all restaurants serve carbonated drinks, which require the use of compressed CO<sub>2</sub> cylinders). It is the goal of our work to use this unique combination of physical and economic properties of CO<sub>2</sub>, in its supercritical fluid state, to enhance the performance of cements containing industrial waste products.

There are two broad areas of application for cements which incorporate industrial waste, and their treatment using supercritical CO<sub>2</sub>. The first is the utilization of solid wastes, generated as by-products of industrial processes, as additives to conventional cements used as building materials. This waste could be flyash from coal fired power plants, amorphous silica filter cake, alum sludge from the deflocculation of drinking water, blast furnace slag, or recycled carpet and paper products.

The second area of application is the enhancement of cement which is itself an industrial waste. By this we mean cemented wasteforms used to immobilize environmentally-regulated heavy-metals and radioactive materials. In order to meet present DOE transportation and storage requirements, cemented wasteforms must satisfy several requirements,<sup>1</sup> including a maximum limit on the radioactive decay heat. Decay heat is defined as the heat produced by radioactive emissions that is absorbed in the surrounding materials. The current decay heat limit is based, in part, on the overall hydrogenous content of the cement. If the hydrogenous content of the cement (which will be primarily water) can be reduced to less than 30 percent by weight, then the maximum allowable decay heat for this modified wasteform increases fourfold.<sup>2</sup> This modified wasteform would not only ensure compliance with transportation and storage regulations, but would reduce the overall amount of cemented waste requiring disposal.

The largest cement samples treated thus far in the SuperScrub™ are 6" diameter x 12" length cylinders, where we achieve nearly complete carbonation (water removal) in a treatment time of several hours. We have found from these experiments that a fully-treated cement permanently sequesters about 130 liters of CO<sub>2</sub> per kilogram of cement. As an example of the changes which can be effected by supercritical CO<sub>2</sub> treatment, Figure 3 shows x-ray diffraction spectra for a 6" x 12" portland cement cylinder which was treated for a length of time sufficient only to produce a reaction in the outer portion of the cylinder. The expected phases, predominantly portlandite, are seen in the spectrum for the inner portion, while the spectrum for the outer portion indicates a nearly complete conversion to calcite. Figure 4 gives the measured compressive strengths and densities for untreated and supercritical CO<sub>2</sub> treated 1" x 2" portland cement cylinders. It can be seen that, for equal curing times, the supercritical CO<sub>2</sub> treatment results in an increased density and increased strength. The strength enhancements serve as a measure of the degree of chemical conversion, while the increased density points to decreased porosity and permeability.

**Figure 3.** X-ray diffraction spectra of the inside and outside portion of a 6" x 12" portland cement cylinder partially reacted with supercritical CO<sub>2</sub>. The circles identify the peaks due to portlandite, while the triangles show the diffraction peaks due to calcite.



#### SUMMARY

We are investigating the use of supercritical fluid CO<sub>2</sub> to produce novel cement-based materials. With appropriate treatment, we are able to incorporate large amounts of industrial waste products, such as flyash, into portland cements, while retaining durability and mechanical strength. This will provide a value-added end use, in the form of building materials, for waste products which currently are sent to land-fills.

**Figure 4.** Compressive strength (solid lines) and density (dashed lines) for untreated and supercritical CO<sub>2</sub> treated Type I portland cements.

We are also applying supercritical fluid CO<sub>2</sub> technology to the enhancement of cemented wasteforms. By accelerating the natural cement-aging reactions, we can improve the overall chemical stability and leaching characteristics of wasteforms. This treatment process will also translate into a reduction in the number of wasteforms destined for disposal.

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# **DESIGN OF SAFER CHEMICALS**



## IRON-COMPLEXED DYES IN POLLUTION PREVENTION

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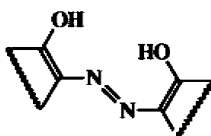
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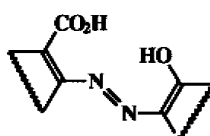
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### ABSTRACT

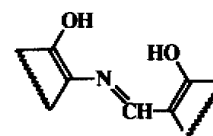
This paper pertains to the design of non-toxic alternatives to currently used metal-complexed dyes containing chromium, cobalt, and copper. Specifically, iron-complexed dyes are described as substitutes for metal-complexed dyes currently used in situations requiring colorants possessing very high photostability and resistance to removal under wet conditions. The dyes investigated are iron (Fe) complexes of ligands of the type illustrated below (**1-3**), and provide the foundation for a pollution prevention approach to environmental problems associated with the use of organic dyes based on metals designated as priority pollutants.



**1**



**2**



**3**

### INTRODUCTION

Metal-complexed dyes are synthetic colorants used most often in applications requiring high stability to prolonged and repeated exposures to sunlight, especially its UV component<sup>1</sup>. These dyes include 1:1 and 1:2 metal:dye complexes that are trivalent chromium (Cr) and cobalt (Co) complexed azo and formazan dyes for polyamide and protein fibers and copper (Cu) complexed azo, formazan, and phthalocyanine dyes for cellulosic fibers. Cr- and Co-complexed dyes are also used as solvent soluble dyes for 1) wood stains and varnishes, 2) inks for jet printing, copying paper, and ball-point pens, 3) fats and waxes for candles and polishes, 4) soaps and cosmetics, 5) petroleum, and 6) mass coloration of molding powders and other construction materials derived from cellulose acetate, vinyl polymers, and phenol-formaldehyde resins. In 1996, more than a million pounds of metal-complexed dyes were produced.

The most important metal-complexed dyes are those synthesized from *ortho*, *ortho'*-dihydroxyazo, *ortho*-hydroxy, *ortho'*-carboxyazo, and *ortho*, *ortho'*-dihydroxyazomethine intermediates<sup>2</sup>. The improvement in photostability following metal complexation occurs by shielding the chromophoric moiety (e.g., azo bond) from electrophilic attack and quenching singlet oxygen formation<sup>3</sup>, while decreased sensitivity to moisture arises from an appreciable decrease in water solubility. In fact, it is clear that metal-complexed dyes are unequaled with regard to their properties in these two key areas<sup>4</sup>.

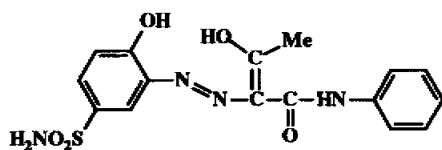
Although a wide range of metals have been examined for their ability to improve the stability of metallizable synthetic dyes, Cr(III), Co(III), and Cu(III) have proved most effective in enhancing the technical properties of azo and formazan dyes in particular<sup>5</sup>. Unfortunately, however, the potential risk these metal ions pose to human health and the environment has led to their becoming classified as priority pollutants<sup>6</sup>.

As an approach to the design of environmentally friendly metal-complexed dyes, our research group synthesized and evaluated two groups of Fe-complexed dyes as analogs of commercial dyes containing Cr or Co ions. We chose Fe(II) sulfate as the metallizing agent because it has exhibited low aquatic toxicity in our studies.

### RESULTS

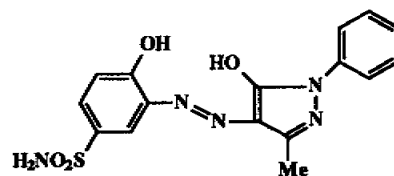
As a starting point for identifying environmentally friendly metal-complexed dyes, our research group synthesized Fe complexes of the most widely used synthetic precursors of metal-complexed azo dyes (e.g., **4-7**), as alternatives to the commercial prototypes, and determined their technical properties<sup>7-10</sup>. All of the resulting Fe complexes gave dyed fibers possessing high resistance to removal by water following their diffusion into wool and nylon fibers. As for photostability, Fe complexes of **4** and **5** gave brownish-yellow colors of moderate

photostability, while dyes from **6** and **7** gave black shades of high photostability<sup>10</sup>. The latter was an important development because it not only provided a new approach to photostable black dyes for protein fibers to consider in



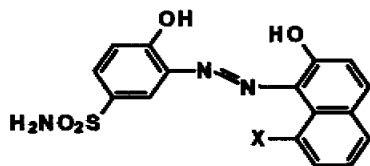
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(Prototype is a yellow 1:2 Co complex)



5

(Prototype is an orange 1:2 Cr complex)



6 (R = H)

(Prototype is a red 1:2 Co complex)

7 (R = NHAc)

(Prototype is a blue 1:2 Co complex)



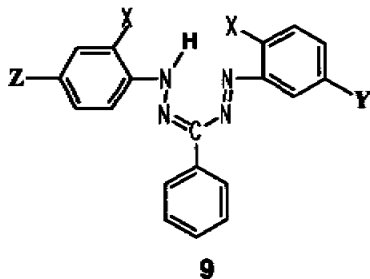
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(Prototype is a black 2:3 Cr complex)

place of the high volume dye CI Acid Black 52 (**8**), it also provided a way to eliminate the use of Cu ions in the manufacturing process associated with this commercial dye. In other words, both the Cr(III) conversion of the unmetallized precursor and the Cu(II) assisted diazotization of 4-hydroxy-7-nitronaphthalene-

1-sulfonic acid, the key step in the manufacture of the precursor, could be discontinued by utilizing the Fe-complexed forms of **6** and **7**.

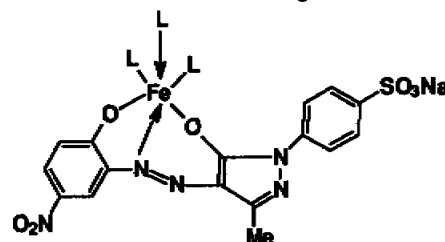
Promising results from studies involving mutagenicity and aquatic toxicity testing of the aforementioned Fe-complexed azo dyes<sup>8</sup> led to an extension of our investigation to dyes containing the formazan system. Although this system is used most often to manufacture dyes that form a covalent bond to cellulosic fibers, there are a few examples of useful metal-complexed formazan dyes for polyamide fibers. In our case, upon synthesizing Fe complexes of **9**, it was determined that several of the dyes possessed remarkable properties. First, like the aforementioned Fe-complexed azo dyes, these dyes generally possessed low aquatic toxicity and were nonmutagenic<sup>8</sup>. Secondly, this series of dyes included members giving photostable black colors on nylon fibers as well as wool fibers<sup>9</sup>. Thirdly, this series included dyes giving blue and violet colors, an observation not reported in the literature prior to our study<sup>11</sup>. Until our study, only brown and brownish-black colors were reported as characteristic of Fe-complexed dyes, and such dyes were manufactured with leather as the target substrate, with CI Acid Brown 98 (**10**) being an important example. Fourthly, we found that ozone-decolorized solutions of our Fe-complexed dyes did not exhibit aquatic toxicity, suggesting that the release of Fe under these conditions does not have an adverse effect on aquatic life<sup>12</sup>.



9

(X = OH, CO<sub>2</sub>H; Y = H, Cl, NO<sub>2</sub>, SO<sub>2</sub>NH<sub>2</sub>;

Z = H, SO<sub>3</sub>Na, SO<sub>2</sub>NH<sub>2</sub>)



10

## SUMMARY

It is clear from the results of our experimental work in this area that the use of Fe in the design of metal-complexed dyes is a viable approach to addressing environmental problems associated with Cr and Co complexed dyes for textile and other end uses. To exploit the potential of this new approach more fully, however, there are several additional types of experiments which need to be performed. This would include the synthesis and characterization of Fe analogs of dyes for cellulosic fibers, as the use Fe in lieu of Cu in metal-complexed dyes has not been undertaken in our own or other published studies so far. Results from these experiments will be used to generate guidelines for designing nontoxic Fe-complexed dyes that: 1) are viable alternatives to currently used metal-complexed dyes, the majority of which are based on toxic heavy metals; 2) possess colors of acceptable brightness and that span the color spectrum; this is an important point because, historically, Fe-complexed dyes have possessed muddy brown colors, severely restricting their utility and appeal; 3) employ



non-toxic metal salts in their synthesis; 4) are relatively inexpensive to manufacture; and 5) take into account the potential genotoxicity of required raw materials.

#### ACKNOWLEDGMENTS

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#### THE DESIGN OF SAFER CHEMICALS: AN OVERVIEW

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As a result of the emphasis on pollution prevention there has emerged a new environmental paradigm known as designing safer chemicals. This concept relates to the systematic design or redesign of industrial and commercial chemicals with the specific intent of making them safe or safer for humans and the environment without substantial changes in their efficacy. The concept also encompasses the means by which molecular manipulation for both safety and efficacy can be integrated into every facet of the development, manufacture, and use of industrial-type chemicals. This presentation will provide an overview of the concept of designing safer chemicals. Specific examples of the successful application of the concept will be discussed.

## THE HIGH LEPIDOPTERAN SPECIFICITY OF TEBUFENOZIDE

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### ABSTRACT

The diacylhydrazine insecticides (tebufenozide, RH-2485 and halofenozide) are novel mimics of insect molting hormone, 20-hydroxyecdysone. These compounds differ somewhat in insect potency and spectrum. However, all seem to exhibit an unusually high degree of target pest selectivity. Tebufenozide, for example, is highly toxic to caterpillar pests (larval lepidopterans) but is essentially non-toxic to other insect types, including a wide range of important beneficial, predatory and parasitic species. Tebufenozide is also relatively non-toxic to other non-target organisms such as mammals, birds, fish and earthworms. Tebufenozide interacts strongly with ecdysone receptors derived from caterpillars, but weakly with similar receptors derived from other insect types. Vertebrates totally lack ecdysone receptors.

### INTRODUCTION

Insects regulate their growth and development through the interplay of juvenile hormone (JH) and 20-hydroxyecdysone (20E, insect molting hormone). Both substances are absolutely critical to the normal functioning of insects but are lacking and/or nonfunctional in most non-insect/arthropod species. Because of this, molecules which selectively mimic or interfere with the action of JH or 20E ought to provide a safer means of insect control. Synthetic analogs of JH, for instance, have been available for several years and are known to be considerably less toxic to vertebrates than older neurotoxic insecticides.

The diacylhydrazines, first discovered in the early 80's, are the first insecticidally active mimics or agonists of 20E<sup>1</sup>. At the present time there are three members of this chemical class in various stages of commercialization or development (tebufenozide, RH-2485 and halofenozide). All exhibit a surprisingly high degree of target specificity.

### PROPERTIES OF TEBUFENOZIDE

Tebufenozide is highly toxic to caterpillar pests but is essentially non-toxic to a wide range of important beneficial insects such as honeybees, parasitic wasps and flies; predatory arthropods, such as ladybird beetles, lacewings, soldier bugs, spiders and predatory mites; and a variety of ecologically important aquatic and terrestrial insects<sup>2</sup>. Tebufenozide also has low apparent toxicity to other non-target organisms such as mammals, birds, fish and earthworms. These properties have made tebufenozide an extremely useful tool for selective control of caterpillar pests in integrated pest management situations.

The low toxicity of tebufenozide to organisms such as vertebrates or earthworms is probably explained by the fact that these organisms do not utilize 20E in any way and do not contain the 20E/tebufenozide target site, which is known to be a heterodimeric complex of two proteins, EcR (ecdysone receptor protein) and USP (ultraspiracle protein). The low toxicity of tebufenozide to non-caterpillar arthropods and insects, on the other hand, seems a more difficult to explain since these organisms, like caterpillars, both utilize 20E to regulate molting and possess similar 20E target proteins.

C-14 tebufenozide feeding studies conducted in our laboratories and elsewhere<sup>3,4</sup> have indicated that the low toxicity of tebufenozide to Mexican bean beetle larvae (*Epilachna varivestis*) and Colorado potato beetle larvae (*Leptinotarsa decemlineata*) can not be explained by poor uptake or transport of parent compound. Such beetle larvae readily absorb tebufenozide from diet and transport it to the epidermis in quantities sufficient to kill caterpillars. Likewise, the rates and patterns of C14-tebufenozide metabolism in these species are very similar to those observed using highly susceptible caterpillar larvae such as southern armyworm (*Spodoptera eridania*) and beet armyworm (*Spodoptera exigua*). Thus, it would also seem that the low toxicity of tebufenozide to *E. varivestis* and *L. decemlineata* larvae can not be explained by enhanced metabolic detoxification.

Competitive ligand displacement assays utilizing tritiated Ponasterone A (a potent 20E-like substance) and EcR-USP heterodimer preparations derived from Indian meal moth (*Plodia interpunctella*) indicate that tebufenozide binds to this representative caterpillar ecdysone receptor with approximately 70 times the potency of the natural hormone, 20E. In contrast, tebufenozide binds to similar receptors derived from the fruit fly (*Drosophila melanogaster*), a weakly tebufenozide-responsive species, with only 0.25 times the affinity of 20E, and to receptors derived from boll weevil (*Anthonomus grandis*) and an Ixodid tick (*Amhlyomma hebraeum*)<sup>5</sup>, two totally non-responsive species, with only 0.02 and 0.0007 times the affinity of 20E, respectively. These binding studies suggest that the unusual caterpillar selectivity of tebufenozide probably arises from the unexpected ability of this molecule to discriminate between EcR-USP receptor sub-types.

## SUMMARY AND CONCLUSIONS

Tebufenozide is toxic to caterpillars because it binds potently to the caterpillar ecdysone receptor complex (EcR-USP) and causes untimely ecdysone-dependent gene expression or inhibition, resulting in molt disruption. The surprising safety of tebufenozide to nontarget insects is probably due to its much reduced ability to bind and activate ecdysone receptors in such insect species. On the other hand, the relative safety of tebufenozide to vertebrates and other non-arthropods is likely explained by the complete lack of the 20E/tebufenozide target site in such organisms.

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# CHEMICAL SYNTHESIS



## POLYMERIZATIONS IN SUPERCRITICAL CARBON DIOXIDE

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### Introduction

Our research program has focused on the use of carbon dioxide as an alternative to traditional solvents for the synthesis of industrially relevant polymers. The reduction and/or elimination of toxic compounds produced during the manufacturing and processing in the chemical industry is a pressing need. Huge amounts of volatile organic compounds (VOCs), chlorofluorocarbons (CFCs), and hazardous aqueous waste streams used as reaction media or in the processing are released as a result of industrial productions. Carbon dioxide is a viable alternative to these traditional solvents. The use of environmentally benign solvents such as liquid or supercritical carbon dioxide would provide an excellent opportunity for a more environmentally responsible chemical industry.

Supercritical carbon dioxide has a number of advantages as a reaction medium. The properties and effects of a supercritical fluid can easily be controlled by changing pressure and temperature. Near the supercritical point, small changes in pressure and temperature result in large changes in density, viscosity, and dielectric constant. Supercritical fluids combine gas phase properties such as high mixing rates, miscibility with other gases, and relatively weak molecular association with liquid properties, particularly the ability to dissolve and transport many organic compounds.<sup>1</sup> Since carbon dioxide is inexpensive, nontoxic, nonflammable, naturally occurring, abundant, easily recycled, and environmentally acceptable and has mild critical conditions ( $T_c = 31.1$  and  $P_c = 73.8$  bar), supercritical carbon dioxide is a viable alternative to traditional solvents. Further, polymers synthesized in carbon dioxide do not have to undergo costly drying or solvent removal procedures.

The dissolving power of carbon dioxide is different for polymers than for small molecules. Generally, if a low molecular weight compound is soluble in hexane then it is soluble in carbon dioxide, but for moderate molecular weight materials with negligible vapor pressures the dissolving power of carbon dioxide is more like a fluorocarbon. Thus many of the industrially important hydrocarbon polymers are insoluble in carbon dioxide and must be synthesized by heterogeneous methods. In contrast, fluorocarbon and silicone polymers are soluble in carbon dioxide and can be synthesized via homogeneous methods.

We have investigated free radical, cationic, step growth, and transition metal-catalyzed polymerizations in liquid and supercritical carbon dioxide. These polymerizations have included homogeneous and heterogeneous (including precipitation and dispersion) as well as carbon dioxide/water phases. This work has shown that environmentally friendly liquid and supercritical carbon dioxide can be used as an effective medium for the synthesis of an array of polymers by using these polymerization methods. We have also developed a method for performing dispersion polymerizations in carbon dioxide by use of a  $\text{CO}_2$ -soluble stabilizer and have shown the importance of proper selection of this stabilizer.

### Results and Discussion

#### *Homogeneous Polymerizations*

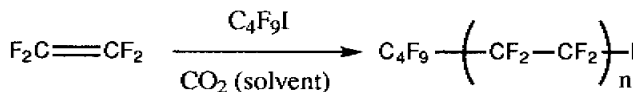
Highly fluorinated polymers are insoluble in organic solvents and are thus synthesized and processed in CFCs. But, the environmental concerns over these compounds requires the search for better solvent. The high solubility of fluorocarbons in  $\text{CO}_2$  make it an attractive alternative solvent for the synthesis and processing of fluorinated polymers. As an example, poly(1,1-dihydroperfluorooctylacrylate) [poly(FOA)], was polymerized homogeneously and the resulting high MW polymer was highly soluble in  $\text{CO}_2$ .<sup>2</sup> A number of fluorinated polymers as well as some copolymers with hydrocarbons were synthesized homogeneously.<sup>2,3</sup>  $\text{CO}_2$ -soluble polymeric amines were also achieved by the copolymerization of FOA with 2-(diethylamino)ethyl acrylate or with 4-vinylpyridine.<sup>4</sup>

Using high pressure UV spectroscopy, we have shown that the 2,2'-azobisisobutyronitrile (AIBN) initiator decomposed 2.5 times slower in  $\text{CO}_2$  than in benzene, but that higher initiator efficiencies occurred in supercritical  $\text{CO}_2$  because of lower solvent cage effects in the lower viscosity supercritical  $\text{CO}_2$  medium.<sup>5</sup>  $\text{CO}_2$  also doesn't react with free radicals and, as such, is a good solvent for free radical polymerizations.

This inertness of  $\text{CO}_2$  to free radicals is exemplified by the telomerization of tetrafluoroethylene (TFE).<sup>6</sup> The highly reactive TFE radicals easily chain transfer to hydrocarbons. We successfully performed the telomerization of TFE in  $\text{CO}_2$  using perfluorobutyl iodide as the telogen; the resulting oligomers had narrow molecular weight

distributions (MW<1.5).

The first homogeneous cationic polymerizations in liquid and supercritical CO<sub>2</sub> involved the use of N-propyl-perfluorooctylsulfonamido ethyl vinyl ether and 1,1,2,3-tetrahydroperfluoroalkyl vinyl ethers.<sup>7</sup> Cationic polymerization at 40 °C using ethylaluminum dichloride as an initiator was performed in CO<sub>2</sub>. Also, the ring opening polymerization of a fluorinated oxetane, 3-methyl-3'(dihydroheptafluorobutoxymethyl)- oxetane, was performed at 0 °C and 289 bar producing similar results as the control experiment run in Freon-113. These results indicate that CO<sub>2</sub> is also a good medium for cationic polymerizations.



#### Precipitation Polymerizations

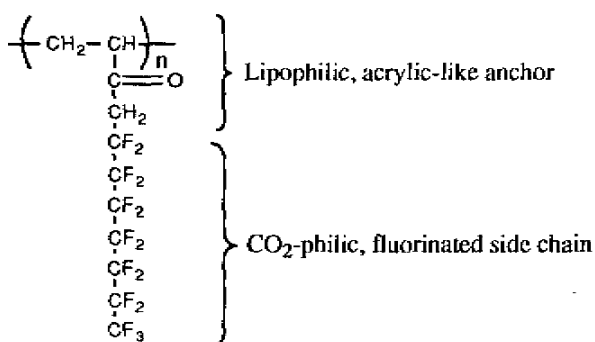
We have studied the precipitation polymerization of acrylic acid in supercritical carbon dioxide and obtained effective molecular weight control using ethyl mercaptan as a chain transfer agent.<sup>8</sup> The polymerizations employed AIBN as an initiator and resulted in greater than 90% conversion.

We have also studied the copolymerization of TFE with perfluoro(propyl vinyl ether) and with hexafluoropropylene in supercritical CO<sub>2</sub>.<sup>9,10</sup> Good yields and high molecular weights are obtained in these reactions, which use bis(perfluoro-2-propoxy propionyl) peroxide as the free radical initiator. The advantages of CO<sub>2</sub> in these precipitation reactions versus the aqueous process include no chain transfer to CO<sub>2</sub>, insignificant formation of undesirable carboxylic acid and acid fluoride end groups which are observed in the aqueous process and can cause processing and performance problems, and the safe handling of TFE as a mixture with CO<sub>2</sub>.<sup>11</sup>

#### Dispersion Polymerizations

The free radical dispersion polymerization of olefins is normally performed in organic or aqueous solvents. Prevention of coagulation or flocculation of colloidal dispersion particles can occur by use of electrostatic, electrosteric, and steric stabilization.<sup>12</sup> Because CO<sub>2</sub> is a low dielectric medium, steric stabilization by polymer chains is the preferred method for dispersion polymerizations in CO<sub>2</sub>. The most effective steric stabilizers are amphiphilic molecules that become adsorbed or grafted onto the surface of the polymer particle by the anchoring segment. The molecules also contain stabilizing segments that are soluble in the continuous phase. The long range repulsions imparted by the stabilizer must be large enough to compensate for long range van der Waals attractions.<sup>13</sup>

Dispersion polymerizations of lipophilic monomers in a supercritical fluid continuous phase can be accomplished



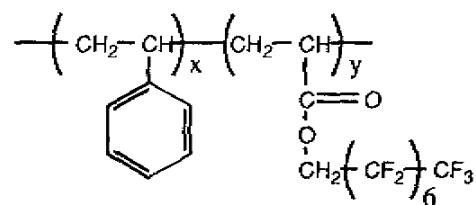
by using steric stabilization.<sup>14</sup> The amphiphilic nature of poly(FOA) was used to stabilize the synthesis of poly(methylmethacrylate) (PMMA). After the reaction was complete the stabilizer was removed by washing the resulting spherical (0.9 to 2.7 μm, characterized by scanning electron microscopy) particles with CO<sub>2</sub>. Very low amounts (0.24 wt %) of poly(FOA) are needed to stabilize PMMA as a latex in CO<sub>2</sub>.<sup>15</sup> Conversions greater than 90% and molecular weights of about 3 x 10<sup>5</sup> g/mol were obtained for these PMMA products. Polymerizations performed in the absence of poly(FOA) resulted in low conversion and low molar masses.

Another effective dispersion polymerization of MMA involved the copolymerization of MMA with a polydimethylsiloxane (PDMS) monomethacrylate, which acted as, the stabilizer.<sup>16</sup> The polymerizations were performed in both liquid and supercritical CO<sub>2</sub> with azo initiators and resulted in spherical particles. Only a small amount of PDMS needed to be incorporated into the polymer to stabilize the particle, and excess PDMS monomethacrylate was removed from the product by washing with hexanes or CO<sub>2</sub>.

The dispersion polymerization technique was also extended to polystyrene.<sup>17</sup> Poly(FOA) was not an effective stabilizer for the dispersion polymerization of styrene, probably because of ineffective anchoring of the stabilizer in the growing polymer particle. Block copolymers consisting of a polystyrene segment, which anchors the stabilizer into the polystyrene particle, and a poly(FOA) block, which is readily solubilized in CO<sub>2</sub>, were synthesized and used as effective stabilizers for the polymerization of styrene.<sup>18</sup> These stabilizers were synthesized by the "iniferter" method employed by Otsu.<sup>19</sup>



The polymerization of styrene in the presence of this copolymer resulted in a dispersion instead of a precipitation polymerization. The polymer was recovered as a dry powder and was in the form of spherical particles. Scanning electron microscopy demonstrated that the product was in the form of submicron sized particles. The size of these particles was dictated by variation in the PS segments and the FOA segments in the stabilizer.



Block copolymers of PS and PDMS were also effectively employed as stabilizers in the dispersion polymerization of styrene.<sup>20</sup> In addition, PS-*b*-PDMS was effective in the polymerization of MMA. The resulting PMMA particles were about an order of magnitude smaller than the particles formed using PFOA as the stabilizer. PDMS alone was ineffective in stabilizing these polymerization reactions.

The cationic dispersion polymerization of styrene in liquid carbon dioxide using amphiphilic block copolymers was also investigated.<sup>21</sup> Block copolymers consisting of a CO<sub>2</sub>-philic poly(fluorinated vinyl ether) segment and a poly(methyl vinyl ether) segment stabilized the growing polystyrene particles. Scanning electron microscopy confirmed the formation of PS particles in the size range of 300 nm to 1 µm in diameter.

## CONCLUSION

This work has shown that CO<sub>2</sub> is an attractive alternative to traditional organic solvents in the manufacture and processing of polymers. Because carbon dioxide is inert to free radicals it is particularly advantageous in free radical reactions. Stabilizers designed for CO<sub>2</sub> open up the possibility of polymerizing a wide array of monomers via dispersion polymerization. The effectiveness of CO<sub>2</sub> as a polymerization medium coupled with its environmental friendliness makes it an obvious choice for future manufacturing of polymers.

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## RECENT ADVANCES IN THE COMMERCIAL SYNTHESIS OF PROGESTERONE FROM SOYA STEROLS

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Though mature, one can still make significant contributions in the field of commercial steroid manufacture. Advances were recently achieved in the soya based synthesis of progesterone at Pharmacia & Upjohn. These improvements arose from the development of a new fermentation process which increases feedstock utilization from 15% to 100%, and the development of a highly selective and green chemical oxidation. Following a brief history of the synthesis of progesterone and details of the bioconversion, the development of a nitroxyl catalyzed sodium hypochlorite oxidation (cf. Anelli, P.L., et al. *J. Org. Chem.* **1987**, 52, 2559) of bisnoralcohol to bisnor-aldehyde will be discussed. The challenges encountered during the rapid development of this oxidation from lab to pilot plant and then full scale implementation will be described, and details of the solutions to them will be given.

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## DIMETHYLCARBONATE AS A GREEN REAGENT

Pietro Tundo

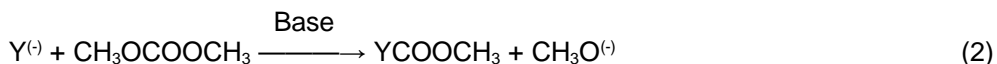
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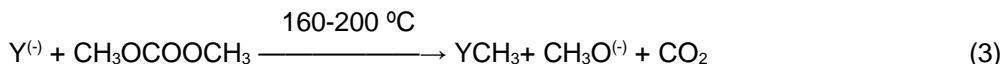
Dimethylcarbonate (DMC) is nowadays produced by the oxycarbonylation of methanol (Eq. 1):<sup>1</sup>



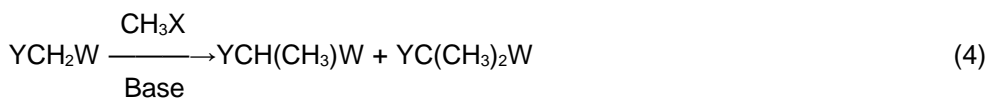
This technology provides a chlorine-free industrial synthesis of DMC which imparts an intrinsic safeness to this reagent. As a primary consequence, the use of DMC is growing more and more in importance as an environmentally safe substitute of the highly toxic phosgene and methyl chloride (or dimethylsulfate) for both carbonylation and methylation reactions, respectively. When reacted with nucleophiles at reflux temperature (90 °C), DMC is a carboxylating agent (Eq. 2):<sup>2-5</sup>



While at high temperatures (>160 °C), it becomes an excellent methylating agent. The methylation reaction prevails over carboxymethylation since the former is not an equilibrium reaction (Eq. 3):



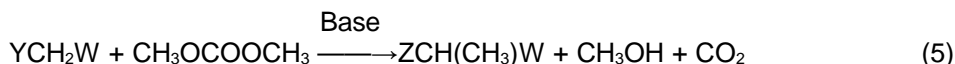
As far as alkylation reactions are concerned, it is well known that especially the direct mono-methylation of methylene-active compounds by common alkylating agents (methyl halides and dimethyl sulfates) is not a facile reaction and generally cannot be run as a one-step process because considerable amounts of dialkylderivatives form (Eq. 4):



Y = Aryl, Aroxy, W = CN, COOR; X = Cl, I, OSO<sub>3</sub>CH<sub>3</sub>

Moreover, especially for large scale preparations, the use of both alkyl halides and dialkyl sulfates poses a serious environmental concern because of the inherent toxicity of such reagents and the unavoidable formation of a stoichiometric quantity of inorganic salts to be disposed of.

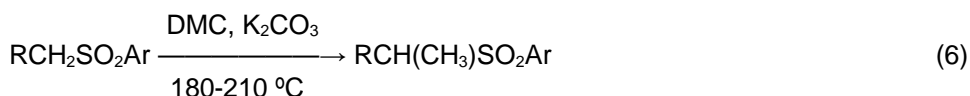
A valuable solution for more selective and safer alkylations can be envisaged by using dialkylcarbonates as alkylating agents, particularly dimethylcarbonate (DMC) for methylation reactions where the selectivity concern is by far more crucial. Thus, highly selective mono-C-methylations of aryl- and aroxy-acetic acid derivatives (nitriles and esters, Eq. 5) are attainable:<sup>6-10</sup>



Base - M<sub>2</sub>CO<sub>3</sub> (M = Li, Na, K, Cs)

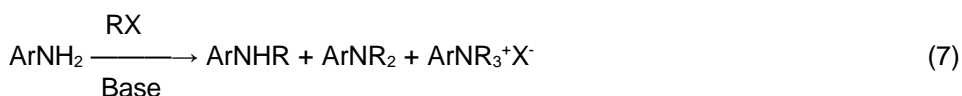
At 180-200 °C, under continuous-flow (Gas-Liquid Phase-Transfer Catalysis, GL-PTC) and batch conditions, typical mono-methyl selectivities are > 99%, at conversion up to 95-99%. Significant examples are the reactions of DMC with (*p*-isobutylphenyl) acetonitrile, 2-(*m*-carboxymethylphenyl)acetonitrile, and methyl (6-methoxy-2-naphthyl)acetate which allow one-pot syntheses of the corresponding 2-(*p*-isobutyl phenyl)propionitrile, 2-(*m*-carboxymethylphenyl)propionitrile, and methyl 2-(6-methoxy-2-naphthyl)propionate in high yields (>90%), respectively. These mono-methyl derivatives are intermediates for the preparation of the well known analgesics Ibuprofen, Ketoprofen, and Naproxen.<sup>6-7,10-11</sup>

Under such conditions, also benzylic sulfones yield the corresponding monomethyl derivatives with as good as selectivities (Eq. 6):<sup>12</sup>

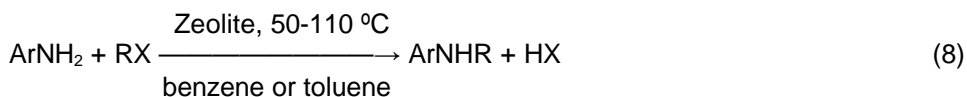


R = Ph, Ar = Ph, *p*-ClC<sub>6</sub>H<sub>5</sub>, *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>5</sub>; R = CH<sub>3</sub>, Ar = Ph, *p*-ClC<sub>6</sub>H<sub>5</sub>, *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>5</sub>

An even more difficult alkylation reaction is the direct mono-N-alkylation of primary aromatic amines. When common alkylating agents (alkyl halides) are used, the reaction has not a synthetic utility because of its poor selectivity; the high nucleophilicity of the aminic nitrogen results in the formation of mixtures of secondary and tertiary amines along with the corresponding ammonium salt (Eq. 7):



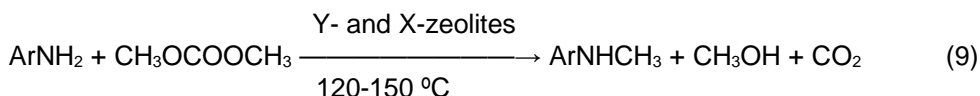
And, although very selective mono-N-alkylations of primary aromatic amines have been reported by using different alkyl halides over X- and Y-type faujasites (Eq. 8), the reaction becomes no longer feasible when methyl halides (or DMS) are involved, because sizable amounts of N,N-dimethyl by-products are obtained.<sup>13</sup>



R = *n*-butyl, allyl, benzyl; X = Br, I;

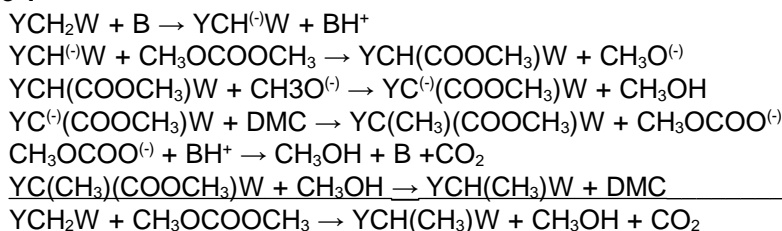
An alternative procedure for selective mono-N-methylations of anilines has been devised by using DMC as the alkylating agent. Accordingly, operating at 120-150 °C, primary aromatic amines are reacted with DMC in the

presence of Na<sup>+</sup> and K<sup>+</sup> exchanged Y- and X-faujasites.<sup>14</sup> Experiments are performed in a stainless steel autoclave with DMC in a very large excess acting as both the methylating agent and the solvent. Both aniline and poorly reactive amines deactivated by electron-withdrawing groups [*p*-O<sub>2</sub>NCH<sub>2</sub>NH<sub>2</sub>, *p*-NCC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, *o*-CH<sub>3</sub>OCC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>] and/or sterically hindered [2,6-(CH<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>NH<sub>2</sub>] yield the corresponding mono-N-methyl anilines [ArNHCH<sub>3</sub>] with a high selectivities (92-97%) at conversions ranging from 72 to 93% (Eq. 9).



As the reaction mechanism is concerned, the high mono-C- and mono-N-methyl selectivity of methylations by DMC is attributable to the occurrence of two consecutive nucleophilic displacements as reported in Scheme 1 for the case of methylene active compounds.

#### Scheme 1



In the presence of a base B (K<sub>2</sub>CO<sub>3</sub>), a carbanion [YCH<sup>(-)</sup>W] initially forms and undergoes a methoxycarbonylation reaction by an attack to the acyl carbon of DMC (B<sub>Ac</sub>2 mechanism). The methoxycarbonyl group (COOCH<sub>3</sub>) increases the acidity of the resulting intermediate [YCH(COOCH<sub>3</sub>)W] thus favouring the formation of the corresponding anion [YC<sup>(-)</sup>(COOCH<sub>3</sub>)W]. This anion, in turn, reacts with the alkyl carbon of DMC to yield the methyl derivative [YC(CH<sub>3</sub>)(COOCH<sub>3</sub>)W] through a B<sub>Al</sub>2 mechanism. Finally, the methyl derivative undergoes a de-methoxycarbonylation reaction to the final product [YCH(CH<sub>3</sub>)W]. The whole reaction uses a catalytic amount of the base since acidity is removed as CO<sub>2</sub>.

This mechanistic pattern might actually also hold for anilines though in this case, the methylation may be assisted by the zeolite cages; K<sub>2</sub>CO<sub>3</sub> being replaced by a basic site of the zeolite. During the reaction, once the amine enters the zeolite cages, the corresponding urethane (ArNBCOOCH<sub>3</sub>) forms and, due to its polarity, is retained inside the cavities where it undergoes both methylation and de-methoxycarbonylation reactions. In particular, the demethoxycarbonylation reaction could be favoured by weakly Lewis acidic sites on the zeolite which seem to be required for the reaction to proceed. Therefore, the unusual mono-N-alkyl selectivity observed is likely attributable to a synergistic effect between the double reactivity of DMC (acting both as a methylating and as a reversible methoxycarbonylating agent) and the dual acid-basic properties of zeolites along with the steric demand by their cavities.

Both N- and C-alkylations by DMC offer a true environmentally benign synthetic alternative to toxic alkylating agents (methyl chloride and DMS) and remarkable environmental benefits are readily recognizable: i) the modern technology of oxycarbonylation of methanol provides a chlorine-free industrial synthesis of DMC which imparts an intrinsic safeness to this reagent; ii) thus, the use of DMC is an excellent starting point to plan methylation reactions which prevent pollution at the source; iii) methylations by DMC are clean reactions: no by-products are obtained except for methanol (recyclable to the DMC production) and CO<sub>2</sub>, and no inorganic salts are produced (alkylations by alkyl halides produce stoichiometric quantity of salts to be disposed of; iv) methylations by DMC allow the use and the develop of eco-friendly catalysts (zeolites), and the utilization of base (alkaline carbonates) in just catalytic amounts. From a synthetic point of view, the reactions of DMC offer unprecedented opportunities of preparing mono-C- and mono-N-methyl derivatives of methylene-active compounds (both arylacetic acid derivatives and α-methylene sulfones) and primary aromatic amines with high selectivity (90-99%) at substantially quantitative conversions.

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### PROGRESS IN NON-COVALENT DERIVATIZATION

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Non-covalent derivatization is the specific application of the principles of molecular recognition and self assembly to control the physical and chemical properties of a molecular species in which auxiliary molecules are added to mitigate the interaction of the target molecules with each other and the surrounding chemical environment. This technique employs non-covalent intermolecular forces [hydrogen bonding, pi-stacking, lipophilic-lipophilic interactions and electrostatic interactions] to trap the molecular species in organized matrices. The procedure of forming molecular assemblies in order to manipulate bulk physical properties allows for reduced usage of chemical resources. Instead of performing several time-consuming, solvent based, chemical reactions in order to synthesize a series of candidate compounds for structure activity studies, non-covalent derivatization allows for the addition of simple, inexpensive, readily available "complexing reagents". For this to be successful as pollution prevention, these assemblies must significantly reduce the number of synthetic reactions carried out. Often the formation of these assemblies involve no organic solvents, the supermolecular structures can be constructed via solid state grinding or aqueous dispersing techniques. Recent applications and investigations into fundamental intermolecular interactions will be presented.



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## CONVERSION OF PAPER SLUDGE TO ETHANOL

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### Project Goals and Objectives

The overall goal of this project is to investigate conversion of waste paper sludge into ethanol and potentially recyclable minerals.

Specific objectives of the project are:

1. Characterize the composition of paper sludges.
2. Characterize, improve, and evaluate continuous simultaneous saccharification and fermentation (SSF) for conversion of pretreated and non-pretreated paper sludge to ethanol.
3. Characterize, improve, and evaluate thermophilic bacteria for continuous conversion of paper sludge to ethanol.
4. Characterize, improve, and evaluate liquid hot water (LHW) pretreatment as a means to increase the fraction of paper sludges that exhibit high conversion to ethanol.
5. Perform measurements on mineral residues pursuant to evaluating their amenability to recycling.

### Technical Approach

This presentation will address aspects of objectives 1, 2, and 3. In particular, we report:

Compositional and low-concentration (2 wt.% cellulose) SSF conversion data (using cellulase from *Trichoderma reesei*) for approximately 40 different paper sludges.

Comparison of low-concentration SSF using alternative microorganisms: *Saccharomyces cerevisiae*, *Klebsiella oxytoca* P2 (genetically engineered to have high ethanol yield)<sup>1</sup>, *Zymomonas mobilis* CP4/pCB5 (genetically engineered to be able to utilize xylose). A particular focus of this comparison will be the ability of these strains to utilize the non-glucose various sugars present in paper sludge (xylose, mannose, galactose, arabinose).

System design and initial results for high-concentration (~ 8 wt.% cellulose) SSF.

Studies of thermophilic bacteria investigating and demonstrating: a) the overall feasibility of consolidated bioprocessing, b) the ability of thermophilic bacteria to utilize high feed substrate concentrations and tolerate produced ethanol (approached using soluble substrates), and c) fermentation of paper sludge by continuous cultures of *C. thermocellum* and *C. thermosaccharolyticum*.

The motivation for studying microorganisms in addition to conventional yeast for paper sludge processing is that yeast is only able to utilize two (glucose and mannose) of the five major sugars present in paper sludge, whereas the alternative microorganisms we are investigating can use some or all of the remaining sugars.

The motivation for studying thermophilic bacteria is that they produce hydrolytic enzymes (cellulases and xylanases) in the course of anaerobically fermenting cellulose at near-zero marginal cost. By contrast, the cost of aerobic production of cellulase in a separate process step (e.g. using *T. reesei*) is substantial and represents a significant barrier to commercialization.

Whereas screening paper sludges for susceptibility to enzymatic hydrolysis is only feasible at low cellulose concentrations (e.g. 2 wt.%), a realistic commercial process will require substantially higher solids concentrations. Operation at higher concentrations requires special equipment because of the physical characteristics of paper sludge.

### Preliminary Findings

The potential value of avoided disposal, conversion to ethanol, and recovery of minerals is about \$270/dry ton, with disposal (at \$30/wet ton) and ethanol production approximately equal and larger than recovery of minerals generally the smallest of the three. (data not shown)

The composition of paper sludges (based on database of 47 different sludges) varies widely, as shown in Table 1.

**Table 1.** Summary of paper sludge composition.

Parameter	# Sludges	Parameter Value (@ given percentile)		
	Tested	25th	50th	75th
% Carbohydrate <sup>1</sup>	40	42.00	59.00	65.20
Glucan	47	35.67	46.82	55.91
Xylan	15	2.49	3.37	5.66
Mannan	15	2.25	2.77	3.02
% Ash	44	12.39	25.41	36.05
% Acid Insoluble Volatile Material	15	12.07	19.38	22.78

<sup>1</sup>Arabinose and Galactose were not analyzed. "Carbohydrate" measured based on glucose + a "hemicellulose sugar peak" to which xylose and manrose contributed with approximately equal sensitivity.

It may be seen that carbohydrates comprise a significant fraction of paper sludge, on average about 50%, with glucan the dominant component.

Similarly, the SSF treatability (using *Saccharomyces*) also varies (Table 2).

**Table 2.** Summary of SSF treatability studies.

	# Sludges	Cellulose Conversion		
	Tested	(% theoretical @ given percentile)		
		25th	50th	75th
7-day conversion <sup>1</sup>	39	63.00	76.73	91.00

<sup>1</sup>Values are calculated from measured ethanol production after a 7-day SSF, reported as % theoretical conversion based on the initial sludge cellulose content as determined by quantitative saccharification and fermentation. SSF as described in the text with cellulase loading = 10-20 FPU/g cellulose; some samples with supplemental B-glucosidase.

25% of the sludges tested gave  $\geq 91\%$  of theoretical cellulose conversion in the absence of pretreatment.

As shown in Table 3, some unpretreated paper sludges are considerably more reactive to enzymatic hydrolysis than are representative pretreated substrates such as dilute-acid pretreated poplar.

**Table 3.** Reactivity comparison for paper sludge and pretreated poplar<sup>1</sup>.

Substrate	% Conversion				
	Paper sludge <sup>2</sup>			Pretreated poplar <sup>3</sup>	
Cellulase	10 U/g	15 U/g <sup>4</sup>	23 U/g <sup>4</sup>	10 U/g <sup>4</sup>	20 U/g <sup>4</sup>
Time (days)					
1.5	54	78	92	29	33
3.0	69	89	96	46	65
6.0	93	98	99	65	91

<sup>1</sup>Results for SSF as described in NREL LAP 008.

<sup>2</sup>Bleached kraft primary clarifier sludge.

<sup>3</sup>Dilute-acid pretreated poplar prepared by the NREL and distributed to subcontractors as a "reference" pretreated substrate for studies of ethanol production.

<sup>4</sup>Cellulase supplemented with 6 U  $\beta$ -glucosidase/U cellulase.

Hemicellulose is hydrolyzed in proportion to cellulose hydrolysis during SSF (data not shown). This has positive implications with respect to the feasibility of paper sludge processing, as hydrolysis of hemicellulose both reduces solid residues and potentially increases ethanol yields. Statistical analyses (not shown) revealed that B-glucosidase supplementation and cellulase loading had a significant positive effect on SSF conversion, whereas the source of the sludge (either recycled vs non-recycled or bleached vs nonbleached) and the growth medium used (yeast extract/peptone vs corn steep liquor) were not significant factors.

Rapid conversion of paper sludge with in situ production of cellulase production has been observed in both fed-batch and continuous culture (Table 4). However, we have also observed slower rates under apparently identical conditions. Current efforts are directed toward resolving this uncertainty.

**Table 4.** Consolidated Bioprocessing of Paper Sludge Using a co-culture of *Clostridium thermocellum* and *Thermoanaerobacter thermosaccharolyticum*

Feed	Cellulose Conversion	Residence Time Equivalent (hrs)	Format
paper sludge @ 10 g/L cellulose + 5 g/L xylose	82%	20-22	Continuous
paper sludge @ 10 g/L cellulose	87%	21	Continuous
paper sludge @ 10 g/L cellulose	91%	16	Sequencing Batch Reactor @ 50 % draw down

While processing insoluble cellulosic materials such as paper sludge is our ultimate goal, certain unresolved questions concerning thermophilic bacteria are most easily approached initially using soluble substrates. These include the ability, or inability, of thermophiles to utilize high feed substrate concentrations, and the related matter of the ability of thermophiles to tolerate high concentrations of produced (as opposed to added) ethanol. We have approached these issues using xylose by *C. thermosaccharolyticum* as a model system. To date, we have produced ethanol concentrations as high as 23 g/L from feed concentrations of approximately 70 g/L xylose. Although higher feed xylose concentrations resulted in washout of the culture, we have demonstrated (data not shown) that this to be due to inhibition by  $K^+$  ion (which accumulates as a result of pH control with KOH) and not due to inhibition by ethanol. Current efforts are directed toward using  $Ca(OH)_2$  as an alternative neutralizing agent in hopes of avoiding cation inhibition and allowing us to further probe product tolerance.

Results concerning use of alternative microorganisms in SSF and high concentration SSF studies are expected to be obtained prior to the June 24 presentation.

### Significance of Findings

Our findings establish several key points that support the overall attractiveness of ethanol production from paper sludge. The finding that a substantial fraction of as-received paper sludges can be enzymatically hydrolyzed to a high extent (Table 2), and that paper sludge reactivity compares favorably to representative pretreated materials (Table 3), implies that paper making is a very effective pretreatment process in some cases, and indicates the potential to avoid the costly pretreatment step characteristic of most cellulosic materials. The effectiveness of commercial cellulase enzymes at hydrolyzing hemicellulose as well as cellulose is also a positive, since this indicates that non-glucose sludge components may well be accessible to fermentation. Finally, the general absence of fermentation inhibition during paper sludge processing is an important indicator of feasibility.

In situ production of hydrolytic enzymes and the ability to rapidly utilize paper sludge at low concentrations substantiate the potential of thermophilic bacteria for this and other applications. As well, utilization of 75 g/L xylose and production of 23 g/L ethanol during thermophilic fermentation of xylose are positive indicators. However, much remains to be done to demonstrate the feasibility of thermophilic processing in this context. Thermophilic conversion, and consolidated bioprocessing generally, should be regarded as a more long-term processing option as compared to SSF.

**Relevance to Vision 2020**

<u>Vision 2020 Component</u>	<u>Responsive Project Element(s)</u>
<i>Biomass</i> "Develop chemistry for use of alternative raw materials [including] efficient conversion of biomass and unused byproducts" (p. 30)  "Very low cost raw materials for bioprocesses will be derived from agricultural and forestry wastes..." (p. 34)	Paper sludge processing could provide a particularly advantageous point of entry for biomass processing technologies
<i>Sustainability</i> Use materials and energy more efficiently. Create products and processes that are environmentally benign. (p. 24)	Overall concept diverts a significant industrial waste into useful products.  Cellulosic ethanol is a potentially sustainable fuel with essentially zero net greenhouse gas emissions.  You can't have a sustainable process without a sustainable feedstock!
<i>Recycling</i> "Many new commercial processes will use recycled raw materials as feedstocks." (p. 41)	The project targets improving the cost effectiveness and environmental impact of paper recycling, which generates sludge in particularly large quantities.
<i>Non-incremental advances</i> Importance of step-change technological improvements recognized (p. 7)	Inclusion of thermophilic bacteria/consolidated bio-processing.

**PRODUCTION OF POLY(HYDROXYALKANOATE) POLYMERS IN TRANSGENIC CROPS**

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**ABSTRACT**

Polyhydroxyalkanoates are storage polymers produced by numerous bacterial species. These polymers also can be used as thermoplastics, and they are currently produced commercially by bacterial fermentation. However, the expenses for fermentation are very high, resulting in a product that is not cost-competitive with petroleum-derived plastics. We are attempting to reduce the cost of polymer production by genetically engineering crop plants to produce polyhydroxyalkanoate.

**INTRODUCTION**

Our laboratory is investigating commercial production of polyhydroxyalkanoate (PHA) polymers in plants. PHA's are normally produced by numerous bacterial species as carbon and energy storage polymers. PHA is accumulated in intracellular granules and may be either a homopolymer, the most common being poly- $\beta$ -hydroxybutyrate (PHB), or a copolymer. Polymer composition is dependent on the intermediary metabolism of the bacterium, the substrate flexibility of the various PHA biosynthetic enzymes, and the carbon source(s) being metabolized.

PHA was originally identified in 1923 (Lemoigne), but these polymers first gained industrial attention in the early 1980's when they were recognized to have thermoplastic properties (King, 1982; Holmes et al., 1981). To date, more than 100 different monomers have been identified, each differing in either the structure of the R-group or the position of the hydroxyl group utilized for polymerization (Stembuchel and Valentin, 1995). The various combinations of homopolymers, copolymers, terpolymers, etc., provide a variety of physical properties, making

each suitable for different applications. Production of polymer containing the appropriate monomer composition and distribution is critical to industrial application of PHAs.

Over the past ten years, the pace of research on PHA's has dramatically increased. The first successful cloning of PHA biosynthesis genes was reported in 1988 (Schubert et al., 1988; Slater et al., 1988). Since then, numerous laboratories worldwide have focused on PHA metabolism, with the resultant cloning and analysis of dozens of PHA biosynthesis genes. We have learned much about PHA production in both native and recombinant systems, and this learning can now be applied to enhance industrial production of PHAs (see Poirier et al., 1995).

The first and only commercial PHA production was initiated by ICI in the early 1980's. The process utilizes *Ralstonia eutropha* (formerly designated *Alcaligenes eutrophus*; Yabuuchi et al., 1995) fed glucose and Na-propionate to produce the copolymer poly- $\beta$ -hydroxybutyrate-co- $\beta$ -hydroxyvalerate (PHBV), which is marketed under the tradename Biopol. The Biopol production process has recently been acquired by Monsanto, and production of Biopol via fermentation is continuing. However, fermentation is an expensive route to production, and Biopol is currently not cost-competitive with petroleum-derived plastics. Selling prices for PHBV today range up to \$7.00/LB for most applications, vs. about \$0.5 for polypropylene. Current production costs for fermentation are high due primarily to the small scale of production (about 1000 metric tons/yr.). However, even at large scale, capital costs for fermentation and harvesting, coupled with substrate costs, make PHBV via fermentation a higher cost polymer vs. other biodegradables (for additional data on biodegradable polymers, see SRI reports, 1994 and 1995).

While the current price is acceptable for a few niche markets, broad utilization of PHA will require significant cost reduction. Biopol cost drivers are currently being optimized, but we believe that the cost to produce PHBV from plants — utilizing existing harvesting and crushing infrastructure — will result in breakthrough cost reduction that will enable selling prices between \$1.00-1.50/lb. At these selling prices, we believe that demand for biodegradable polymers will be substantial — 100's of millions of lbs. Thus, we are attempting to engineer plants to produce PHA, with particular focus on our currently-marketed polymer, Biopol.

We are building on the work of Chris Somerville's laboratory, who demonstrated production of PHB in transgenic *Arabidopsis* (Poirier et al., 1992; Nawrath et al., 1992). They determined that PHB production was tolerated within the chloroplast, and achieved PHB concentrations up to about 15% of cell dry weight without significant additional phenotypic effects. We are using both *Arabidopsis thaliana* and *Brassica napus* (canola) as model systems, with canola serving as a model for production of PHA in the leukoplasts of seeds. In both cases, the proteins are being targeted to the plastids.

In extending the previous work, our primary challenge is metabolic engineering of plants to produce the PHBV copolymer. The Biopol fermentation process feeds propionate, a substrate required for  $\beta$ -hydroxyvaleryl-CoA formation, directly to the bacteria. However, production of PHBV in plants requires deriving all necessary precursors from plant intermediary metabolism, so a novel pathway was required. A proposed pathway is diagrammed in Figure 2. Propionyl-CoA is derived from threonine via  $\alpha$ -ketobutyrate. The remaining reactions, catalyzed by  $\beta$ -ketothiolase, acyl-CoA reductase, and PHA synthase, utilize enzymes from the PHA pathway of *R. eutropha*. The particular  $\beta$ -ketothiolase used, BktB, is an enzyme discovered in our laboratory that is capable of forming both  $\beta$ -ketovaleryl-CoA and acetoacetyl-CoA. The need for this new enzyme came from our discovery that PhbA, the  $\beta$ -ketothiolase utilized in previous transgenic plants, was extremely inefficient at forming  $\beta$ -ketovaleryl-CoA.

The threonine deaminase in our experiments is IlvA of *E. coli*. IlvA is on the biosynthetic pathway from threonine to isoleucine, and is normally feedback-inhibited by isoleucine. To avoid inhibition of IlvA, we are utilizing IlvA mutants that are, to varying degrees, insensitive to isoleucine.

We have analyzed the proposed PHBV production pathway in recombinant *E. coli*, and determined it to be functional (Table 1). The level of C5 (hydroxyvalerate) monomer in the polymer is dependent both on the *ilvA* allele used, and on whether threonine is provided in the culture medium. These same genes have been transferred to plants, and we are preparing to analyze the resulting lines. We expect results within the next several months.

## SUMMARY

This project performs several functions for Monsanto. PHAs are biologically-produced, biodegradable

thermoplastics, and are therefore a sustainable product capable of replacing many petrochemically-derived polymers. It is precisely this type of product that is targeted by Monsanto's vision of sustainable development. In addition, this project provides a potential means to reduce costs for a current Monsanto product, while we learn a great deal about metabolic engineering of plants to produce commodity products. We expect that much of the current learning will be applicable to other projects, and we hope to extend this work to develop additional PHA copolymers in plants.

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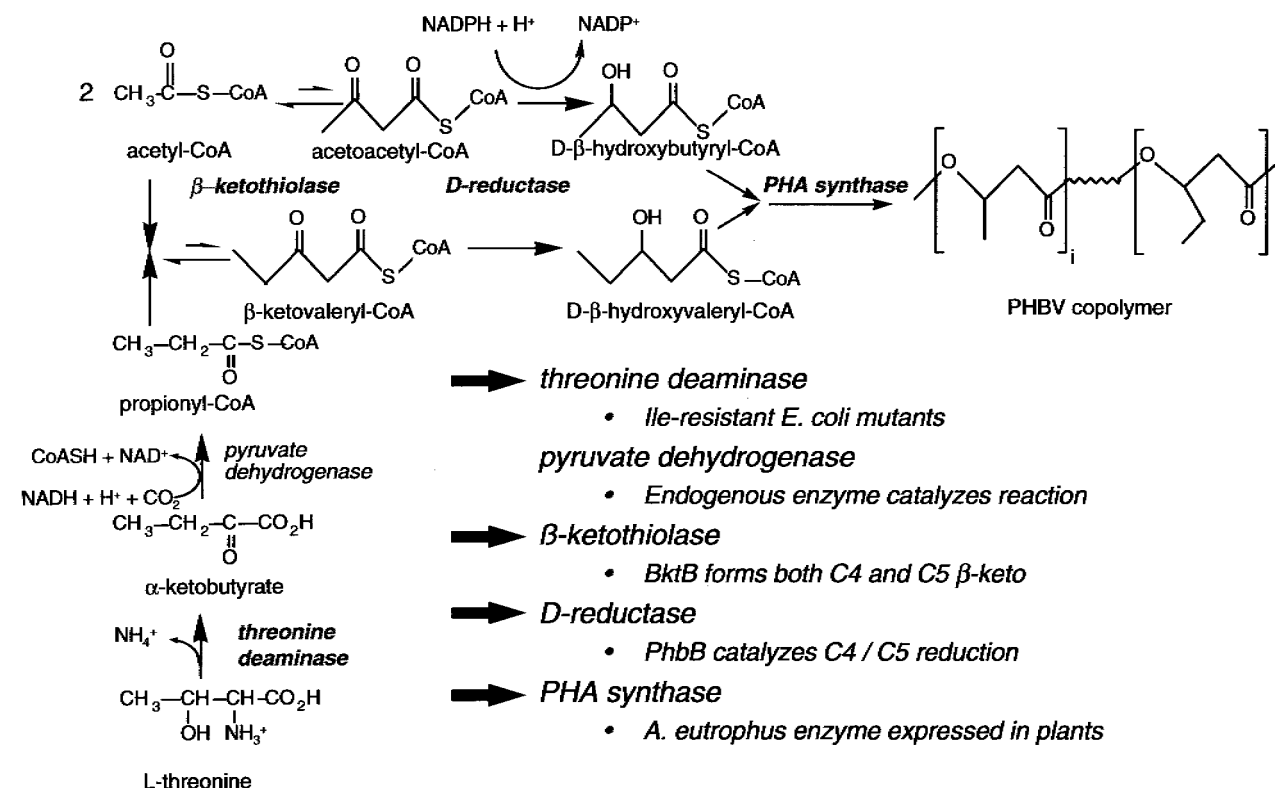
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**Table 1.** Production of PHBV in *E. coli* expressing *IlvA* (threonine deaminase), *BktB* ( $\beta$ -ketothiolase), *PhbB* (AACoA reductase), and *PhbC* (PHA synthase).

Plasmid <i>ilvA</i> <sup>1</sup>	Threonine added? <sup>2</sup>	mol% Hydroxyvalerate
none	yes	3.5
none	no	not detected
<i>ilvA466</i> (L481F)	yes	31.4
<i>ilvA466</i> (L481F)	no	7.9

<sup>1</sup>All cells expressed *ilvA*<sup>+</sup> from the chromosome.

<sup>2</sup>Threonine concentration in media was 10 mM.



**Figure 1.** Proposed PHBV pathway for plants

## PRODUCTION OF A BIODEGRADABLE ROAD DEICER FROM WHEY PERMEATE

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### ABSTRACT

Experimental studies were conducted for the bioconversion of lactose and biomass wastes such as whey permeate to organic chemicals that can be utilized in the production of a road deicer substitute for rock salt. Results indicate that an overall conversion rate of 90% to 99% can be achieved with a two-stage fermentation system utilizing *Lactobacillus plantarum* in the first stage, followed by *Propionibacterium acidipropionici* in the second stage. High product acid yields and high acid concentrations of about 40 g/l to 60 g/l have been obtained in batch, fed-batch, and continuous fermentation runs.

### INTRODUCTION

The effective utilization of biomass and residuals from agricultural and food processing operations is one of the cornerstones of policies aimed at energy conservation and sound environmental management. Biomass wastes such as liquid whey effluents are an undue burden on the environment due to their high biochemical oxygen demand. Treatment of these wastes to meet environmental standards is both capital and energy intensive. This paper will examine the utilization of whey permeate in the production of calcium magnesium acetate and calcium magnesium propionate as substitutes for sodium chloride as a road deicer. Currently used deicers cause extensive corrosion related damage to the highway infrastructure and environmental damage by contaminating water supplies and soils. The main objectives of this research are to examine the use of biomass wastes in the production of calcium magnesium acetate (CMA) and calcium magnesium propionate (CMP), via a two-stage bacterial fermentation process, and to model continuous cell-recycle fermentation in coculture systems.

### TECHNICAL APPROACH

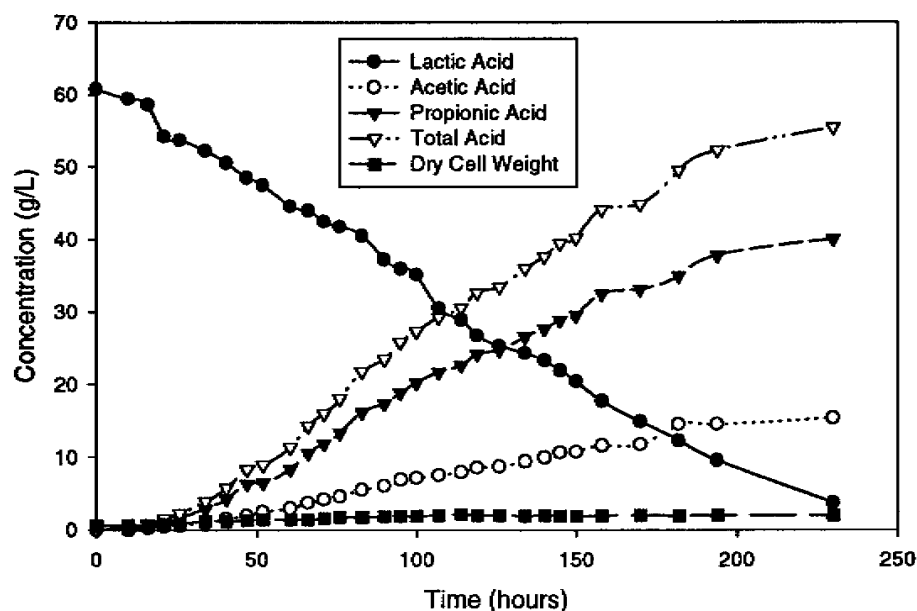
Fermentation studies have been conducted in two stages using *Lactobacillus plantarum* in the first stage and *Propionibacterium acidipropionici* in the second stage for the generation of organic acids used in the production of the deicer. The experimental program was designed to evaluate single and two-stage systems to produce the required organic acids at a high conversion rate and at high final acid concentrations. A high conversion rate will minimize the need to separate unutilized substrate from the product stream. A high product acid concentration will reduce the downstream processing costs involved in producing the deicer.

### RESULTS AND DISCUSSION

The effects of pH, substrate concentration, and oxygen have been evaluated for lactic acid fermentation using *L. plantarum*, and the data have been analyzed using a Monod cell growth model. Both lactose and whey permeate were used as substrates. Lactic acid production was observed even at pH 4, and the optimum pH range was found to be 5 to 6. Anaerobic fermentation gave lactic acid yield about 2.3 times higher than for aerobic fermentation.

Single stage fermentation studies were conducted for the conversion of lactose to propionic and acetic acids using *P. acidipropionici*. With a starting lactose concentration of 40 g/L, batch fermentation over a period of 190 hours gave a total acid concentration of about 20 g/L. The overall conversion rate is only about 60% due to the loss of carbon dioxide in the metabolic pathway. In the two-stage process, lactose and whey will be converted to lactic acid using *L. plantarum* followed by the conversion of the product to acetic and propionic acids using *P. acidipropionici*. The results obtained to date indicate that an overall conversion rate of 90% to 99% can be obtained with a two-stage process.

Experimental data for the fermentation of lactic acid to propionic and acetic acids are shown in Figure 1. These



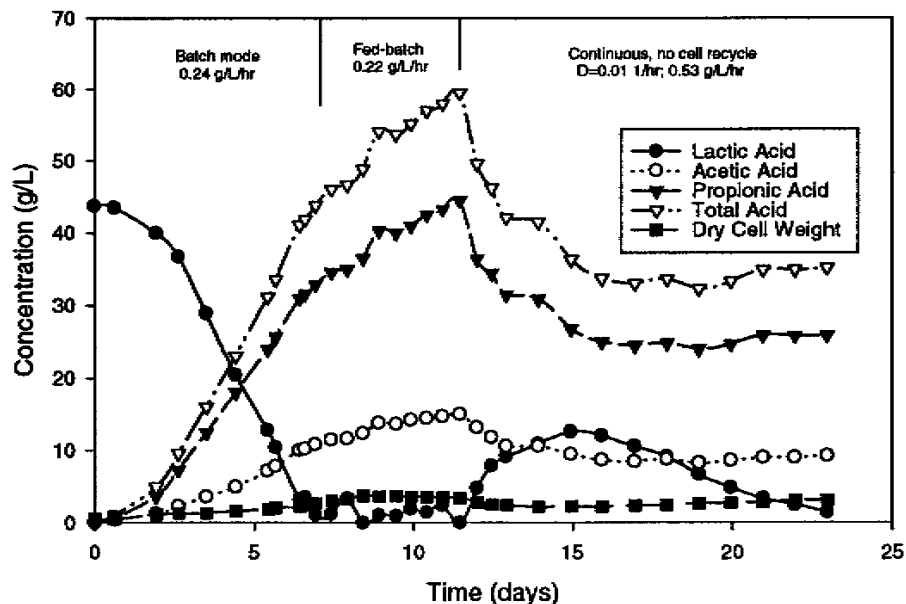
data indicate that, in addition to a high conversion rate, a high product acid concentration of about 60 g/L can be maintained in these systems. Batch, fed-batch and continuous fermentation experiments were conducted for the conversion of lactic acid by *P. acidipropionici*. The results, shown in Figure 2, indicate that acid productivity can be increased by changing from batch to fed-batch and continuous modes of operation. At a dilution rate of 0.01/hr, the acid concentration was maintained at about 40 g/L with a productivity of 0.53 g/L/hr.

**Figure 1.** Lactic Acid Fermentation by *P. Acidipropionici* P200910

## SUMMARY

Sodium and calcium chlorides are at present most commonly used for road deicing in winter. CMA that is produced currently from synthetic acetic acid is about 20 to 30 times more costly than rock salt. As a result, the use of CMA by highway and road management agencies has been quite limited. The results from this study indicates that a two-stage fermentation system can be effectively utilized in the conversion of biomass and other organic wastes to produce a low-cost deicer. The concept and process presented support the goals of Vision 2020 by providing a new bioprocess technology that will utilize low-cost raw materials that are a burden on the environment. Moreover, by aiding in the economic production of deicer that is less corrosive, infrastructure repair and maintenance costs will be reduced substantially.

**Figure 2.** Batch, fed-batch, and continuous fermentation of lactic acid by *P. Acidipropionici*





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# SEPARATIONS



## REACTIVE DISTILLATION SYSTEMS FOR WASTE REDUCTION AND PRODUCTIVITY IMPROVEMENT

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### Abstract

Reactive distillation is an emerging technology with the potential to make quantum leaps in productivity in some sectors of the chemical industry. One of the key aspects of the technology is the potential for improved raw materials usage by increased reaction selectivity, thereby reducing or eliminating waste at the source. Systematic geometric methods are being developed to rapidly identify feasible reactive distillation systems. This is the simplest possible approach that still preserves essential information on the complex interrelations among operating conditions, phase behavior and chemical reaction rates and equilibria. The approach successfully screens out infeasible designs, and provides such information as catalyst placement, feed positions and flows, etc for feasible designs. Experimental testing and validation of the approach has been achieved for equilibrium reactive distillation.

### Project Goals and Objectives

This research is focused on combining chemical reaction and distillation technology which are often traditionally done separately. This hybrid combination is sometimes called "catalytic" or "reactive" distillation. This technology is broadly applicable as the basis for innovative process designs that improve yields and productivity and eliminate or reduce by-product formation. Applications include:

- Fuel additives and substitutes, e.g., in the manufacture and purification of alcohols and ethers such as ethanol, methyl tert-butyl ether (MTBE) and dimethyl ether (DME). The specific potential impact would be in the well-recognized national needs for cost-effective cleaner fuels.
- Innovative process designs in the chemical and petroleum industries to improve productivity and reduce solvent and energy use, e.g., in the manufacture of various esters (Agreda and Partin, 1990).

It is known that reactive distillation is feasible in several applications, but it is not known how to decide effectively when this technology will be attractive. In fact, it is important to point out that this technology is not always desirable and not generic in terms of a process configuration. For example, the necessary arrangements for feeds and products, locations and amounts of catalysts, holdups, etc., change from case to case. The feasible process configurations generally combine reactive distillation with non-reactive distillation components and these depend critically on the combined effects of phase behavior, reaction chemistry, equilibria and rates. Depending on the characteristics of the mixture and the desired products, reactive distillation can actually be inferior to traditional approaches and may even be infeasible. However, there are many applications where reactive distillation is a superior technology over more traditional processing.

The specific goal of this research is to provide experimental testing and validation for existing theories of equilibrium reactive distillation. Although aspects of these theories have been used in practice for nearly a decade, they have never been compared with experimental data in the open literature. We also anticipate confirming the existence of a *reactive azeotrope* (a mixture that boils and reacts at a constant composition) in a real mixture for the first time. Such confirmation would constitute a new discovery, leading to a significant advance in our understanding of equilibrium reactive distillation systems.

We also expect this project to lead to new theories of kinetically-controlled reactive distillation systems, with simultaneous experimental testing. This research has the potential to lead quickly to new technology and new processes for reduced waste formation and improved productivity in many areas of chemical technology by combining reactions and separations that are often done in separate steps.

We have new theories and modeling tools for conceptual design of reactive distillation systems, either already available or currently under study with research support from other sources, including industrial partners. The theory suggests a basic concept for experiments, which is to determine the *residue curve map* for a reacting mixture in order to rapidly assess the feasibility and potential for reactive distillation.

### Technical Approach

New design and synthesis methods and new computational tools for nonideal mixtures have been developed in

recent years. The early work focused on cases without chemical reaction (see the reviews by (Doherty and Knapp, 1993; Malone and Doherty, 1995; Widagdo and Seider, 1996)) and later with equilibrium chemical reactions (Barbosa and Doherty, 1988). More recently, studies including chemical reactions with kinetics (Doherty and Buzad, 1992; Venimadhavan et al., 1994; Rev, 1994) have appeared. These approaches are often termed *geometric methods* because they represent the thermodynamics and conservation equations simultaneously either on phase planes or in the phase space for systems with 3 or 4 degrees of freedom or using tools such as bifurcation diagrams for systems in higher dimensions, e.g. (Fidkowski et al., 1993).

One of the major recent accomplishments for equilibrium reactive distillation was the discovery that chemical reactions can induce the formation of constant-boiling, reacting mixtures or "reactive azeotropes" that *do not* exist under non-reactive conditions, and that they can also destroy the presence of azeotropes that *do* exist when reactions are absent. Both events can occur simultaneously, as happens in reacting mixtures of isobutene, methanol and methyl *tert*-butyl ether (MTBE). In this system the chemical reaction eliminates the azeotropes between methanol and MTBE, and methanol and isobutene. It simultaneously creates a new (reactive) azeotrope between all three components that is very rich in MTBE (Doherty and Buzad, 1992; Venimadhavan et al., 1994; Rev, 1994).

The presence or absence of these reactive azeotropes is critically important in the invention of feasible flowsheet alternatives for achieving the desired products. For a chemical reaction of the form  $v_A A + v_B B \rightleftharpoons v_C C$ , a reactive azeotrope will form at any point where the following thermodynamic condition is satisfied

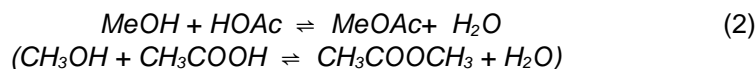
$$\frac{x_A - y_A}{V_A - V_T x_A} = \frac{x_B - y_B}{V^B - V_T x_B} \quad (1)$$

This condition has also been generalized successfully to cases with multiple reactions and to mixtures containing an arbitrary number of components as well as an arbitrary number of inerts, solvents, etc. (Ung and Doherty, 1995b; Ung and Doherty, 1995a). Although the theory of equilibrium reactive distillation has been studied in detail, there are no systematic experimental studies published in the literature. In this project we are experimentally measuring residue curves for equilibrium reactive mixtures.

### Preliminary Findings

Conceptually, residue curves can be found from measuring the liquid phase compositions as a function of time in an isobaric open evaporation. At low pressures, a setup in glassware is generally sufficient. Samples of various initial compositions are boiled and the composition of the liquid is measured periodically (Yamakita et al., 1983); some studies have also measured the corresponding vapor compositions (Bushmakin and Kish, 1957). This approach can measure a single residue curve for each feed composition and along the portion of the residue curve from the initial composition to the stable node. For reacting mixtures, the catalyst level and the heating rate may also influence the residue curves (without reaction, the heating rate influence only the duration of the experiment, but not the residue curves.) These factors alone make an intimate connection between modeling and experiments essential.

The esterification of methanol (*MeOH*) with acetic acid (*HOAc*) to methyl acetate (*MeOAc*) is used here for model testing and validation, viz.

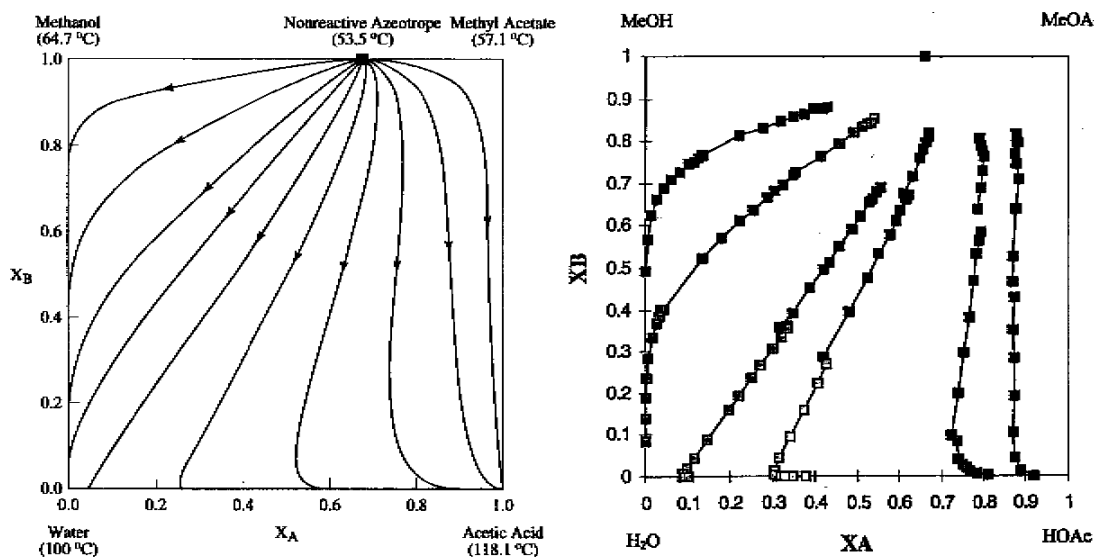


In our recent work initiating experimental studies of reacting mixtures, we have focused the limiting case of both chemical reaction equilibrium and phase equilibrium for which there are also fairly well-developed theories. With four components at phase and reaction equilibrium, two *transformed* composition variables are independent, e.g.,  $x_A = x_{\text{HOAc}} + x_{\text{MeOAc}}$  and  $x_B = x_{\text{MeOH}} + x_{\text{MeOAc}}$  (Ung and Doherty, 1995b; Ung and Doherty, 1995a). The basic approach is to measure the liquid compositions and portray the results in terms of these transformed variables.

The theoretical prediction for this case is shown in Figure 1 (Barbosa and Doherty, 1988). The binary azeotrope between methanol and methyl acetate survives the reaction and this is the lightest "component" or *unstable node*, acetic acid has the highest boiling point and is a *stable node*, and both methanol and methyl acetate are intermediate boiling *saddles*. There are no *distillation boundaries* in the map, and it is feasible to produce high purity methyl acetate and water in a single column that combines extractive and reactive distillation.

The experimentally determined residue curve map is shown in Figure 1. For these 10 data sets, 48 g of catalyst were used in an initial liquid volume of ca. 400 ml. The total amount of liquid removed by sampling for each run was 10 to 15 ml. Initial conditions closer to the *MeOH-MeOAc* azeotrope were not possible with this catalyst on account of the moisture content of the Amberlyst 15, which is necessary for activity.

Figure 1 shows very good agreement with the equilibrium theory and experiments at high catalyst concentrations. We believe that this is the first report of measurements for residue curve maps in reacting mixtures and the first experimental test of fundamental theories that form the basis of geometric methods for process design and synthesis.



**Figure 1.** Residue curve map (left) predicted by the equilibrium theory of Barbosa and Doherty (1988) and (right) according the measurements described in the text.

### Significance of Findings

The results of initial experiments described above show good agreement between the equilibrium theory and experiments in one example for a single reaction. The equilibrium theory also allows the possibility of a reactive azeotrope and strongly suggests that these can form in a variety of cases. An understanding of the presence or absence of these constant-boiling, reacting mixtures is vital to the use of this technology, but even their existence has not been demonstrated experimentally. To our knowledge, there have not yet been any experimental studies of systems with multiple reactions, despite their obvious impact on selectivity. Theoretical studies of the effects of kinetics on residue curve maps for reactive distillation have begun, with some intriguing results, but there have been no experimental tests published.

### Relevance to "Technology Vision 2020"

This research relates to the goals described in "Technology Vision 2020" as follows:

1. *Improved chemical synthesis.* On p. 29, "synthesis" is defined as, "the efficient conversion of raw materials into more useful molecules." Reactive distillation is capable of improving the efficiency of raw materials conversion by improving selectivity by the unique combination of reaction with separation.
2. *Improved process science and engineering technology.* On pp. 39-40 there is specific mention of the need for improved engineering design, process synthesis, and conceptual design. There is also specific mention of the need to improve yields, reduce waste, and have higher capital utilization. One of the technologies identified for achieving these goals is, "integration of reactor and separation systems such as reactive distillation." This research addresses all these issues.
3. *Shorter times from concept to manufacturing.* One focus of this project is to develop models to guide experiment. This aspect addresses the goals cited on p. 44, "designing analytical strategies that minimize

the number of measurements required for definitive laboratory measurements," and on p. 73, "shorter times from concept to manufacturing." The integration of theory, computation, and experiment that we propose will reduce R&D times and put the chemical industry in a superior competitive position.

### Acknowledgement

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## SEPARATIONS RESEARCH AT USEPA: MEMBRANES AND ADSORPTION FOR RECOVERY OF VOCs AND ORGANICS

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### INTRODUCTION

To achieve a sustainable world, there is increasing pressure to move towards multimedia zero emissions industrial processing. Separations technologies enable process lines to more closely approach zero emission through in-process recycling and reuse of resources that would otherwise be emitted to air, water, and solid wastes. More needs to be done however to improve options for separations and make technologies more efficient and user friendly. Mature separations technologies like distillation have been around for over 100 years; others have a much shorter history. Technologies like adsorption, extraction, membrane processes and hybrid processes offer areas of research opportunity for improving resource recovery. As energy costs increase, alternatives to distillation such as membranes and adsorption become more attractive. However, the knowledge

base regarding these newer technologies is limited and needs to be expanded with basic and applied research to further advance separations processes which in turn will encourage industry adoption. This view is consistent with the recommendations for research contained in the chemical industry's *"Technology Vision 2020: the US Chemical Industry"*. Under *Enabling Technologies, Process Science and Engineering Technology* (PS&ET) the report specifically calls for "nontraditional" separations systems research.<sup>1</sup>

ORD-NRMRL scientists and engineers are building on their existing expertise in separations technologies for removal of organics and metals from wastestreams to new applications in direct recycling and recovery in industrial process streams. This area of research is a logical evolution for an environmental engineering laboratory whose past focus in command and control technologies is changing to one of pollution prevention. In our group at EPA's National Risk Management Research Laboratory we have recently completed two projects in remediation oriented separations. We are now extending this work to potential industrial applications for in-process recycling.

### **PERVAPORATION FOR VOLATILE ORGANIC COMPOUND (VOC) RECOVERY**

Background. Pervaporation is a membrane process in which a liquid containing two or more components contacts one side of a non-porous polymeric membrane while a vacuum or gas purge is applied to the other side. Components in the liquid stream sorb into the membrane, permeate through the membrane and evaporate into the vapor phase, hence the name pervaporation. The vapor, referred to as permeate, is then condensed. Literature concentration factors range from single digits to over 1000, depending on the compounds, the membrane, and process conditions. Advantages over conventional air stripping/activated carbon processes are that there are no fugitive emissions, no regeneration costs, and the VOCs can potentially be recovered for reuse.<sup>2</sup>

Pervaporation to recover surfactant in a contaminated groundwater cleanup process. After several years of bench scale work with pervaporation processes using simulated and actual contaminated streams, our first pilot scale testing of the technology came with a Department of Defense project. Five thousand gallons of surfactant-based soil remediation fluid containing VOCs from a test plot at Hill Air Force Base in Layton, Utah were transported and treated at EPA's Cincinnati pilot unit which was equipped with, at first, spiral wound and, then, hollow fiber pervaporation modules. The VOC contaminated groundwater also contained an anionic surfactant (Cytec MA-80) present at 2.4 wt%, isopropyl alcohol present at 1.5 wt%, and approximately 2000 mg/l sodium chloride. At a feed flow rate of 0.25 gallons per minute, 50 deg C feed temperature, and 55 torr permeate pressure, up to 96% 1,1,1-trichloroethane, 95% trichloroethylene, and 88% tetrachloroethylene was removed in a single pass through the four commercial spiral wound modules. The average feed concentrations for the demonstration were 400 mg/l 1,1,1-trichloroethane, 2800 mg/l trichloroethylene, and 400 mg/l tetrachloroethylene. Similar results were seen with the hollow fiber membrane modules; however, operational advantages of the hollow fiber modules made them the module of choice for scale-up.

Novel membrane development. A novel elastomeric membrane for recovery of VOCs from industrial aqueous streams has been developed in our laboratory. The new membrane can achieve a separation factor of 3000 for TCA at concentrations up to 450 mg/l. This is a 30% improvement in the separation factor of 2300 of a commercial silicon membrane used for TCA separation from water. When toluene was tested, separation factors of 3500 to nearly 6000 were seen at feed concentrations between 50 to 300 mg/l. Additional experiments using TCE showed separation factors of between 4000 and 6000 at concentrations of 50 to 300 mg/l in the feed. Permeate concentrations increased with increasing feed concentrations and at the highest feed concentration, 300 mg/l, 50 wt% and 60 wt% toluene and TCE were achieved, respectively. Generally the VOC flux was similar to commercial membranes, while the water flux was lower, hence the improved selectivity. A patent application is in progress for the new membrane and it is currently being tested in electronic chip manufacturing for removal and recovery of both VOCs and ultrapure water.

Software development. In 1996, NRMRL began the development of the Pervaporation Performance Prediction Software and Database (PPPS&D). The software program will assist in predicting the performance of pervaporation processes for user-selected conditions as well as provide a database of performance characteristics of membrane materials reported in the literature for commercial and research membranes. Plans are to beta test a preliminary version by Fall, 1997.

Future directions. In November, 1996, NRMRL hosted a workshop in Cincinnati to discuss the potential for pervaporation in industrial organics recycle. About twenty participants from academia, government and industry

drafted a list of research needs. The recommendations included the need for development of new membrane and module materials which are capable of withstanding harsh industrial environments, for example, development of modules for amine dehydration. Another recommendation was to investigate in-process recycle of certain industrial streams, such as acetic acid in pulp manufacturing. Another potential application is in chemical synthesis processes where pervaporation would be used to remove reaction products, thereby pulling the equilibrium to the product side and increasing yields, as for example, in removal of water in esterification processes.

For the near future our work will pursue several avenues which directly build on earlier work with recovery of surfactants from groundwater remediation streams. One line of investigation will be to look into possibilities for increasing surfactant yields in surfactant manufacturing operations. Another proposed study would evaluate pervaporation in recovery of alternative metal surface cleaning compounds where limonene and isopropanol are targets.

### **ADSORPTION FOR METALS RECOVERY**

Previous work. In 1996 we began an in-house research program to identify low-cost, highly selective adsorbents for recovery of copper and lead. This work forms the nucleus of an in-house program directed to the recovery and in-process recycle of copper, nickel and chromium in the printed wire board and electroplating industries with possible extension to mining and primary metals manufacturing industries. Although this program was narrowly focused on remediation applications initially, the capabilities and methods that are being developed will have pollution prevention applications.

Our early research for low cost lead and copper adsorbents screened a variety of inexpensive alternatives, for example 1) forestry and pulp industry byproducts, such as steam exploded wood and lignin 2) modified granular activated carbon (GAC) 3) granulated tires 4) hydroxyapatite and 5) chitosan beads. Many of these are powdered materials with particle sizes from 10  $\mu\text{m}$  to 100  $\mu\text{m}$ . Multi-stage mixer-settler operations with these materials would be cumbersome due to the small particle size and slow settling velocity. To circumvent this problem, we demonstrated that it is possible to immobilize materials in a reticulated polyurethane foam (RPF) matrix and still retain metal binding capacity. A carboxymethyl lignin derivative (CML), carbon black, and hydroxyapatite were immobilized in RPF at 30-40% mass loading. At 30% loading, the RPF-CML composite had a capacity of approximately 120 mg Pb/g RPF-CML (12 wt% loading). Further improvement in the derivitization of lignin could easily double the projected capacity. The RPF-CML adsorbent cost is approximately \$1.60/lb.

Pilot-scale demonstration. In September, 1996, EPA and NASA conducted a joint pilotscale soil washing/adsorption study at a small arms firing range. Several soil washing solutions comprised of sodium acetate and nitric acid were evaluated for their lead leaching ability. An additional objective of the study was to evaluate two ion exchange materials for their ability to remove lead from the soil washing solution so that it may be recycled back to the process. One ion exchange material was the EPA-developed RPF-CML discussed above, and the other was a NASA-developed ion exchange material made from polyacrylic acid entrapped in cross-linked polyvinyl alcohol beads. The pilot unit consisted of two 0.8 ft<sup>3</sup> columns, operated at a flow rate of 1 gpm and successfully removed lead from the soil wash solution. The estimated cost to treat the soil wash solution was \$26/1000 gallons and \$60/1000 gallons, for the RPF-CML and NASA material respectively. Although adsorbents were not regenerated in the pilot scale demonstration, regeneration of these same materials was demonstrated in the laboratory. The lab-scale regeneration studies indicated that costs could be significantly reduced if regeneration were employed in the field.

Current and planned research. In our studies on materials for copper and lead recovery we are also investigating how these materials perform in the presence of chelating compounds such as citrate and EDTA commonly used in the metal finishing industry. Preliminary results indicate that the inexpensive modified lignins do not have the adsorptive capacity of commercial resins, however they maintain more adsorptive capacity in the presence of chelates and require less acid to regenerate as compared to commercial resins. We are also evaluating how adsorptive capacity changes over repeated adsorption/regeneration cycles, and additional column experiments are planned to develop relative cost data for copper recovery. Selectivity of the new adsorbents for lead, copper, cadmium and zinc in multi component solutions is also being established.

A type of in-process recycling system, integrating ion exchange and electrowinning, will be demonstrated by recovering copper from an electroless copper rinse water and recycling both copper and water back to the metal finishing process. The project will evaluate conductive ion exchange polyurethane foam electrodes developed by the EPA. Although the focus of this work is on near zero-discharge electroless copper plating processes, for



comparison, part of our studies may involve rinse water from electroless nickel plating. The foam based ion exchange electrode technology is generic and compatible with virtually any type of ion exchange resin or material.

## SUMMARY

Separations research at USEPA is being redirected from remediation applications to inprocess recycling applications, making separations research a cornerstone of in-house pollution prevention research. The focus of our pollution prevention research in the past has been on source reduction through substitution of less toxic chemicals and processes. However, in cases where more environmentally benign substitute chemicals and chemical processing methods are either not available or are not accepted by the manufacturing community, separations technologies which allow industrial processes to approach zero emissions are needed immediately. In addition, even in cases where processes have been modified by substitution of cleaner chemicals, there will be a need to insure resource conservation through near zero emissions processing.

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## CLEAN SOLVENT EXTRACTION USING POLYETHYLENE GLYCOL-BASED AQUEOUS BIPHASIC SYSTEMS

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## ABSTRACT

In aqueous biphasic systems (ABS), the major component in each of the two immiscible phases is water, and thus a liquid/liquid extraction technology can be envisioned which completely eliminates the use of volatile organic compounds (VOCs). Elimination of VOCs has the potential to revolutionize many industrial processes by drastically reducing potential downstream pollution while increasing safety. This presentation will discuss our research efforts to obviate the need for VOCs in many separation and waste remediation technologies by the development of ABS into useful systems for the selective batch or chromatographic removal and recovery of solutes and particulates.

## INTRODUCTION

"The goal of Technology Vision 2020 is to enable the (chemical) industry to continue to lead in technology development, manufacturing and profitability, while optimizing health and safety and ensuring environmental stewardship"... One area of opportunity for new chemical science and engineering technology which will help meet this goal is the development of new separations technologies that eliminate the use of flammable, toxic VOCs as solvents. Used in conjunction with, or instead of appropriate current manufacturing processes, such technologies would help to prevent pollution and increase safety. New separations technologies developed for pollution prevention may also find application in pollution remediation, helping to clean up already contaminated sites.

Traditional solvent extraction employs partitioning of a solute between two immiscible phases, typically an organic solvent and an aqueous solution. The ability to utilize a number of different diluents, extractants, and aqueous phases makes solvent extraction a powerful separations method possessing a number of favorable characteristics including rapid extraction kinetics for many separations, the adaptability of the method to a wide variety of solutes, and back extraction or stripping of the solute and recycling of the solvent and/or diluent are often feasible. Further, liquid/liquid extraction is capable of large volume throughput and is amenable to large-scale separations, and can be engineered for high selectivity and efficiency by the use of multistage contactors.

In spite of these numerous advantages, there are several drawbacks to traditional oil/water solvent extraction. Even with today's environmental standards a number of extraction systems still utilize toxic and flammable organic diluents. When the diluent is coupled with a highly selective extractant the cost of the solvent system can become very expensive. (Not to mention the costs of safely designing a system to operate with a volatile or flammable diluent and the high costs of disposal.)

Aqueous biphasic systems consist of two immiscible phases formed when certain water soluble polymers are combined with one another or with certain inorganic salts in specific concentrations. As two-phase systems they are suitable for carrying out liquid/liquid separations of various solutes such as biomolecules, metal ions, and particulates<sup>1-3</sup>. In ABS *the major component in each of the two phases is water*, and because of this non-denaturing environment these systems have been widely employed in biological separations for over 40 years. It was surprising to us, however, that a liquid/liquid extraction technology that holds the possibility of completely eliminating the use of VOCs has been virtually ignored for all separations except biomolecules.

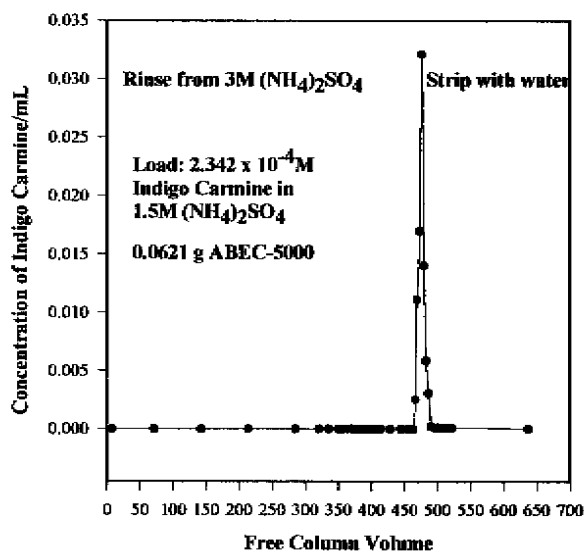
ABS retain all of the practical advantages of liquid/liquid extraction and also have a number of unique advantages due, in large part, to their aqueous nature. Polyethylene glycol (PEG)-based ABS are virtually nontoxic and nonflammable, all components are commercially available in bulk quantities and are inexpensive, and the systems have reasonable phase separation characteristics and can even be used with traditional solvent extraction equipment. In addition, the PEG-rich phases in PEG-ABS appear to be tunable; their phase characteristics can be changed to match the hydrophobicity and water content of a number of organic solvents.

## SUMMARY

The long range goal of this project is to obviate the need for VOCs in many industrial separation and waste remediation technologies by the development of ABS into useful systems for the selective batch or chromatographic removal and recovery of solutes and particulates. This goal includes: a) development of a fundamental understanding of the factors governing solute partitioning in ABS, b) understanding phase behavior in ABS in order to attain the ability to fine-tune the PEG-rich phase and thus solute partitioning, c) expanding the uses of ABS by targeting applications suited to this technology, d) gaining an understanding of the relationships between liquid/liquid ABS separations and solid-supported chromatographic ABS separations, and e) full adaptation of ABS into both liquid/liquid and solid-supported aqueous biphasic extraction technologies.

We have had several successes during the course of our research in this area<sup>4</sup>. These include: a) the separation and recovery of  $\text{TcO}_4^-$  from  $\text{MoO}_4^-$  in a variety of salt solutions, b) the separation and recovery of  $\text{TcO}_4^-$  from simulated Hanford tank wastes (Figure 1), c) the separation and stripping of soft metal halide complex anions from sulfate solutions, d) proving that extraction with ionophores capable of metal ion recognition is possible in PEG-ABS, and e) successful adaptation of many of these metal ion separations with PEG-ABS to an Aqueous Biphasic Extraction Chromatographic (ABEC) mode<sup>5</sup>. During the course of these studies many correlations between system variables and partitioning behavior have led to a better understanding of the factors governing partitioning in ABS<sup>6</sup>. More recently, we have adapted ABEC separations to the removal of color from textile wastes (Figure 2). Many dyes and metal dye complexes partition from salted effluents to the ABEC resins. The

dyes can typically be recovered by washing the resins with water.



This presentation will review our results to date and discuss the challenges in implementing ABS or ABEC technologies. Target industries for these technologies will also be discussed in terms of pollution remediation and pollution prevention. Realization of our long range goals will lead to cleaner, cheaper, safer, and better separations technologies than are currently available for a variety of applications. Elimination of VOCs has the potential to revolutionize many industrial processes by drastically reducing potential downstream pollution while increasing safety. In addition, certain separations where traditional oil/water techniques are not applicable or perform poorly, may be successfully carried out utilizing ABS.

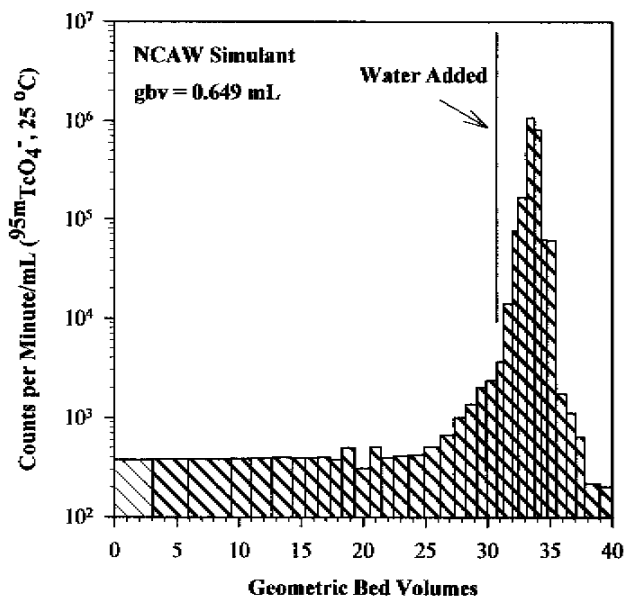
FIGURE 1. Elution curve for Indigo Carmine on ABEC-5000.

## ACKNOWLEDGEMENTS

The portions of this research dealing with metal ion separations are funded by the National Science Foundation (Grant CTS-9522159). The research directed toward organic molecule separations is supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy (Grant No. DE-FG02-96ER14673).

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**FIGURE 2.** Chromatographic separation of  $^{95m}\text{TcO}_4^-$  from Hanford Tank NCAW waste simulant using ABEC-5000.

## TRANSFERRING IONS FROM ONE LIQUID PHASE TO ANOTHER: FUNDAMENTAL PRINCIPLES AND THEIR APPLICATION TO NUCLEAR-WASTE SEPARATIONS WITH CROWN ETHERS

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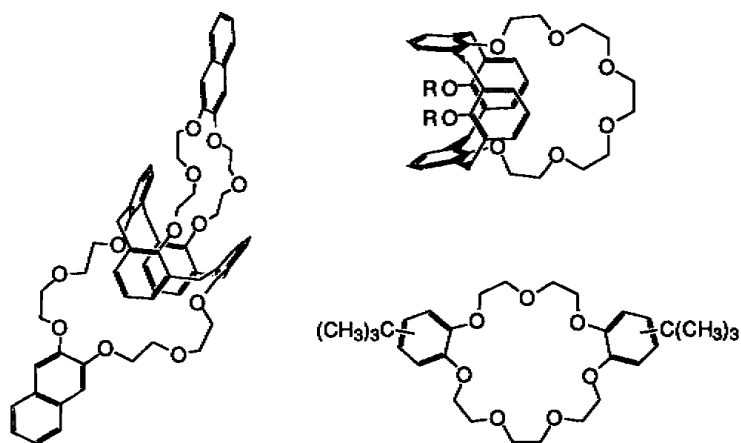
The field of liquid-liquid extraction, commonly called solvent extraction, has grown extensively in the past half century to become an economically significant family of techniques in industry, analytical chemistry, and research. Precisely because of its usefulness, liquid-liquid extraction has continued to evolve in terms of physical configuration (e.g., solvent extraction, liquid membranes, and extraction chromatography) and chemistry. Some of the major developments have in fact been driven by the needs of pollution prevention and include the use of sophisticated and highly selective extractants.

Historically, industrial-scale solvent extraction has its roots in the nuclear industry, as related to the recovery of uranium and thorium from ores and the reprocessing of irradiated nuclear fuels. Even in its early development, solvent extraction was recognized to offer substantial advantages in waste minimization. For example, the replacement of precipitation processes with solvent-extraction processes such as PUREX reduced waste production in nuclear separations by well over an order of magnitude.<sup>1</sup> Now, the legacy of nuclear-weapons production lies before us in the form of stored radioactive wastes and contaminated sites. In the USA, highly

radioactive wastes stored in underground storage tanks at Hanford, Idaho Falls, Savannah River, and Oak Ridge await treatment and ultimate safe disposition. As the USDOE turns from Cold War priorities to dealing with such "tank wastes" and other legacy matters, considerable investments are being made in developing new technologies and deciding among treatment options. Whether consciously or not, technologists and decision makers have often been applying green principles in this regard, preferring options that consume less raw materials and produce lower waste volumes, sometimes even when the needed technologies have not yet been proven viable. Tank wastes in particular represent an excellent case in point. At the former plutonium-production site at Hanford, Washington, 55 million gallons of highly alkaline wastes are stored in underground tanks.<sup>2</sup> Although the entire bulk of this waste could be mixed with glass frit and vitrified, the cost of such a massive operation together with subsequent geologic storage of the resulting increased waste volume would be prohibitively expensive. Instead, a more rational approach recognizes that less than 0.1% of the mass of the waste is in the form of harmful radionuclides and that separation of this small, high-level fraction from the waste can greatly reduce the overall cost while concentrating the hazard into a more manageable volume.<sup>3</sup> How to achieve this worthwhile end has been the subject of intensive research for the past 5-10 years at several USDOE facilities.

In our own laboratories, we are testing the feasibility of using solvent extraction to remove the key radionuclides <sup>99</sup>Tc, <sup>90</sup>Sr, and <sup>137</sup>Cs from the Hanford waste solutions.<sup>4</sup> This had effectively been proposed in a scheme exploiting largely known processes for removing radionuclides from acid solution.<sup>5</sup> It was our thought, however, that it would be advantageous to develop new solvent-extraction methods capable of removing the contaminants directly from the alkaline waste, thereby obviating the addition of a huge quantity of acid. As discussed widely in the literature, crown ethers hold some promise as selective extractants for the removal of the Cs and Sr from nuclear waste.<sup>6</sup> Figure 1 depicts three representative types of crown compounds proposed for extraction of Cs<sup>+</sup> ion from nuclear wastes. Various substituted calix[4]arene-crown-6 and calix[4]arene-bis-crown-6 compounds have been reported to possess Cs/Na selectivities in excess of 10<sup>4</sup>.<sup>7</sup> X-ray structures have shown that these compounds are highly preorganized and enforce a cation-arene pi interaction in a well-defined cavity.<sup>8</sup> Lipophilic crown ethers derived from dibenzo-21-crown-7 are also selective for cesium, but since Cs/Na selectivities are

"only" 10<sup>2</sup>, these compounds cannot match the performance of the calix-crown-6 compounds under the severe test posed by the Hanford tank waste.<sup>9</sup> Increased selectivity effectively translates to a reduced high-level waste volume, because the degree to which competing ions such as Na<sup>+</sup> are co-extracted is greatly reduced.



**Figure 1.** Representative crown compounds potentially useful for the selective separation of Cs<sup>+</sup> ion from nuclear waste: *alt*-calix[4]arene-bis-(2,3-naphtho-crown-6) (left), 1,3-dialkoxy-calix[4]arene-crown-6 (upper right), and bis-(*t*-butylbenzo)-21-crown-7 (lower right).

It is important to recognize that, in addition to high selectivity for Cs, a major advantage of crown ethers lies in the reversibility of the extraction. Equilibrium analysis of the extraction process shows that the driving force on extraction derives from the high nitrate concentration in the waste.<sup>10</sup> A key reaction is simply formation of the 1:1 complex:



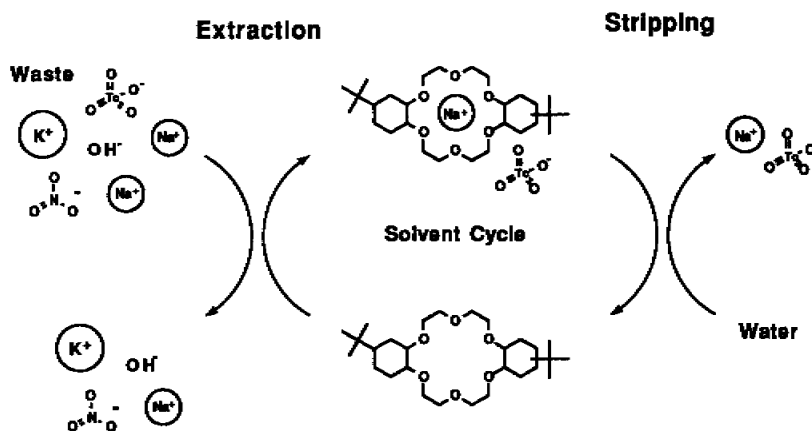
If the resulting solvent loaded with cesium nitrate is then contacted with water, the equilibrium reverses in accord with mass action.<sup>9</sup> The water can then be evaporated or passed through ion-exchange columns to concentrate the contaminants without the addition of chemicals. Overall, the process potentially offers good separation of the contaminant from the waste, high concentration factor, and low secondary waste, all essential "green" properties when dealing with nuclear waste. This process may be contrasted with other methodologies employing ion-exchange principles, whereby stripping may be effected only by treating the solvent or ion-exchange material with high concentrations of chemical stripping reagents. One is then left with another separation problem and large secondary waste production associated with further processing of the stripping solution.

Removal of the radionuclide  $^{99}\text{Tc}$  from the waste poses a different chemical problem, in that much of the Tc in the waste is in the form of the tetraoxo anion pertechnetate ( $\text{TcO}_4^-$ ). Crown ethers do not complex pertechnetate directly, but it is easy to see from Eq. 1 that, like nitrate, pertechnetate could function as the extracted co-anion to preserve charge neutrality in the overall ion-pair extraction. In a recent review article,<sup>11</sup> we evaluated a number of relevant factors such as electrostatics, solvent cohesion, and hydrogen bonding. These principles dictate that the transfer of ions from water to an organic solvent environment generally favors ions having small charge-to-radius ratio, and this selectivity rule indeed persists in anion-transfer and exchange processes. Since pertechnetate has a smaller charge-to-radius ratio and correspondingly lower hydration energy than the inorganic ions such as hydroxide, nitrate, nitrite, chloride, sulfate, and carbonate abundant in the waste, separations based on this simple principle can effect the needed separation of pertechnetate from the waste. Indeed, it has been possible to develop a process based upon a crown ether to remove Tc as pertechnetate from alkaline nuclear waste. Called SRTALK, the process features the favorable water stripping discussed above and thus has the "green" benefit of minimal secondary waste production.<sup>12-14</sup> As shown in the scheme in Fig. 2, SRTALK employs the crown ether bis-(*t*-butylcyclohexano)-18-crown-6 as the preferred extractant (among many tested)<sup>13</sup> for sodium (and also potassium), which is abundant in the waste. Although nitrate represents a competing ion, practical selectivities on the order of  $10^3$  for pertechnetate vs. nitrate have been attainable in solvents composed of an aliphatic kerosene (Isopar® L) containing polar modifiers such as tributylphosphate (TBP).

Further improvements can be obtained by tailoring the solvent-extraction system to separate more than one radionuclide at a time. We showed that under certain conditions SRTALK simultaneously separates  $\text{Sr}^{2+}$  and  $\text{TcO}_4^-$  ions from alkaline nitrate media.<sup>13</sup> Likewise, we have noted the co-extraction of  $\text{Cs}^+$  and  $\text{TcO}_4^-$  ions from alkaline nitrate solutions. In both examples, the crown compound binds the target cationic contaminant, accompanied by the anionic co-contaminant  $\text{TcO}_4^-$ . It has even been possible to show that Cs, Sr, and Tc can be simultaneously extracted in a single step.

A "suite" of radionuclide separation processes applicable to alkaline nuclear waste has now reached the development stage.<sup>4</sup>

**Figure 2.** Depiction of the SRTALK process for separation of Tc as pertechnetate anion  $\text{TcO}_4^-$  from alkaline crown ether forms a large lipophilic cation upon binding sodium (or potassium) ion, and pertechnetate trans phase as the preferred co-anion. Stripping is easily effected with water or a dilute electrolyte solution.



### Acknowledgment

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## SEPARATIONS - AN INDUSTRIAL PERSPECTIVE TO POLLUTION PREVENTION

David W. Savage

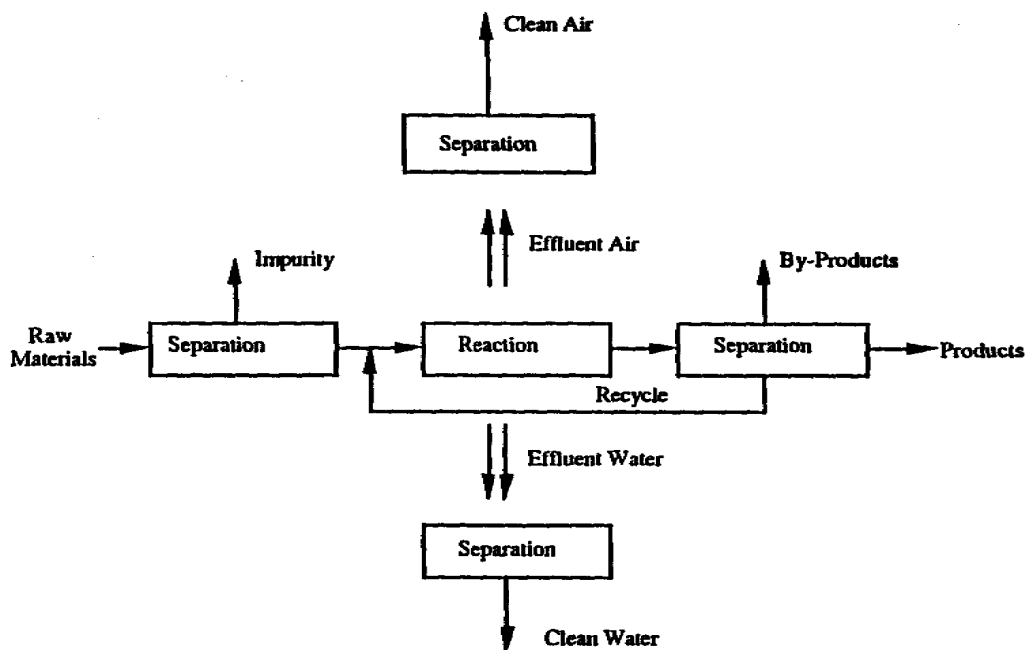
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### ABSTRACT

This paper presents a brief introduction and overview to the session on separations from an industrial perspective. It highlights areas such as combined reaction/separation, separations from dilute solutions and generating high selectivity among solutes where research advances are needed to reduce waste and prevent pollution.

### INTRODUCTION

Separation processes are key enabling technologies for achieving technology vision 2020 in the U.S. chemical industry. Figure 1 illustrates the major roles that separation processes play in typical manufacturing operations today. In the transformation of raw materials to products, separations are important for removal of impurities from feed-stocks, and for separating reactor effluents into main products, by-products and recycle streams. Separation processes also play a major role in reducing or eliminating emissions to air and water.



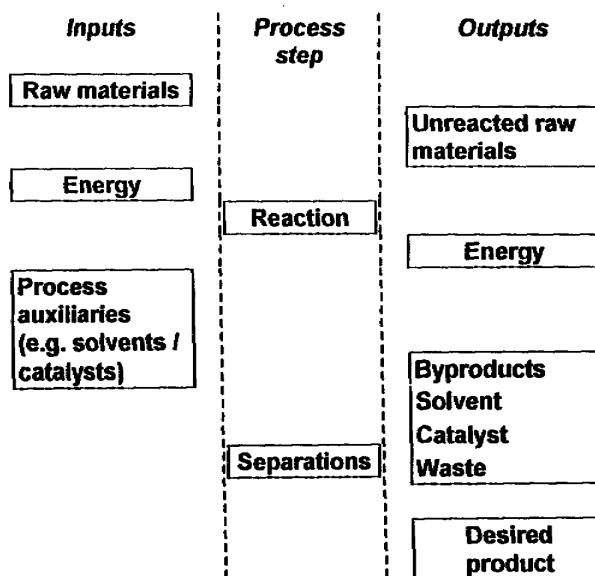
**Figure 1.** Separation Processes In Manufacturing

Pollution prevention and waste elimination require broad thinking taking into account multiple factors such as separation process performance, cost, energy requirements and environmental considerations. The relationship among these factors is illustrated in Figure 2. From a waste elimination point of view the process is more than just raw materials transformation to desired products by reaction and separation. Consideration must be given to energy inputs and outputs, and key process auxiliaries such as solvents and catalysts. On the output side consideration must be given as unreacted raw materials, unwanted by-products, spent solvents and catalysts, and other wastes.

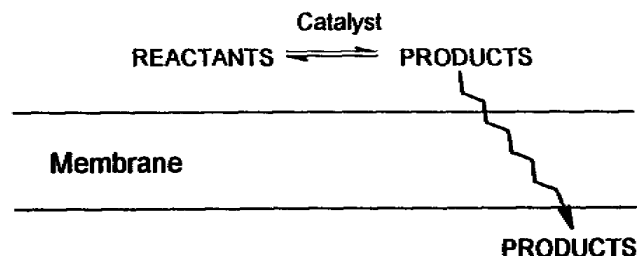
### POLLUTION PREVENTION RESEARCH

The talks in the session will emphasize three major themes which are important in pollution prevention:

Combined reaction/separation. Reactive (catalytic) distillation is a relatively new technology for combining reaction and separation to obtain improved productivity, lower costs and waste reduction. This technology came about as a result of advances in catalytic structured packings, and understanding of how to closely integrate vapor-liquid equilibria, thermal effects and catalytic chemistry and kinetics. It has already been adopted widely by industry for the manufacture of methyl t-butyl ether, the gasoline oxygenate MTBE, and in a different form for esterification to make methyl acetate. The key challenge for the future in catalytic distillation is to improve our understanding of this complex process so that the technology can be extended to a wider range of applications.



**Figure 2.** Separations: Pollution Prevention / Waste Management

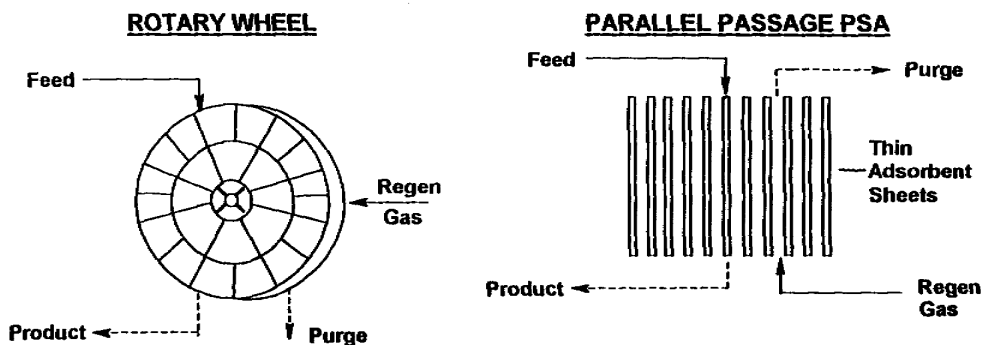


Another promising possibility for combining reaction and separation is a membrane reactor, in which a reaction is combined with membrane separation, as illustrated in Figure 3.

**Figure 3.** Combined Reaction / Separation

The membrane is chosen so that the reaction products permeate selectively through the membrane. This can lead to higher yields, by shifting the equilibrium. It can also lead to fewer secondary reactions, and hence fewer unwanted by products. The key future challenge is to develop robust, thin permselective membranes. These will likely be inorganic membranes owing to the high reaction temperatures involved.

Separations from dilute solutions. Making efficient separations from dilute solutions is a challenging problem because of the large amount of fluid that must be processed to remove a minor constituent from the stream. Many gas separations involve large volumetric flows at low pressure, and hence here is a need for separation processes that offer low pressure drop. Important advances in materials science and engineering science are leading to promising new contactors for dilute gas separations, as illustrated in Figure 4.



**Figure 4.** Separations From Dilute Solutions

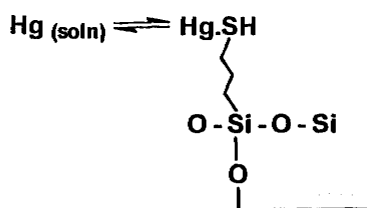
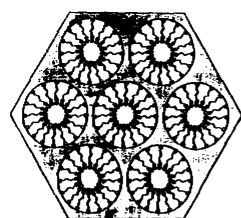
One of these is the rotary adsorbent wheel which is gaining industrial acceptance for air pollution control applications. The wheel, comprising monolithic adsorbent, rotates slowly moving the adsorbent between cool adsorbing and hot regeneration zones. Another emerging low pressure drop technology is the parallel passage pressure swing adsorption (PSA) process, which uses monolithic or thin adsorbent sheets.

Membranes continue to make inroads, especially for gas separations. For liquid phase separations pervaporation is a promising technology but advances are needed to avoid membrane fouling and improve module design. In general, membrane processes do not scale up well, and their use may be limited to smaller scale applications.

Biosorption, in which micro-organisms are used to decompose contaminants in an engineered contactor, represents a low cost approach which is receiving some industrial attention for removal of water-soluble VOC's.

Generating high selectivity among solutes. The third theme is that of generating high selectivity among solutes. The underlying science is sometimes referred to as molecular recognition using mass separating agents. Examples include aqueous biphasic systems and crown ethers. Both of these are at the research stage and show considerable promise for dealing with important national problems involving metal cations and anions.

Another interesting example, reported recently in the literature, and illustrated in Figure 5 uses reactive sorbents that act by weak reversible chemical reaction. The separating agent is a mesoporous silica with functionalized monolayers containing thiol groups. These pick up metal ions such as mercury from aqueous solutions, with partition coefficients in excess of 10 to the fourth.



**Figure 5.** Generating High Selectivity Among Solutes...Molecular Recognition

## CONCLUSIONS

Multiple approaches are needed to move us towards technology vision 2020. The many problems we face are unlikely to be solved by just one or two technologies. Thus a vigorous research program needs to be maintained. The challenge for the future is to develop robust separating agents that offer high selectivity and capacity for contaminants, and can be readily regenerated for re-use.

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**PROCESS  
ANALYTICAL  
CHEMISTRY**



**ADAPTABLE IN-SITU CHEMICAL SENSORS FOR MONITORING IN LIQUID AND GAS STREAMS**

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The Center of Process Analytical Chemistry (CPAC) at the University of Washington has an ongoing program to investigate an adaptable chemical sensor platform for process and environmental monitoring. The sensor integrates traditional reagent based chemical analysis techniques, fiber optic spectroscopic detection, and membrane sampling in a compact, rugged system for monitoring of a variety of analytes in liquid and gas streams. By using selected reagent based chemistries for specific analytes, the response of a given sensor can be adapted for different applications without extensive hardware modifications.

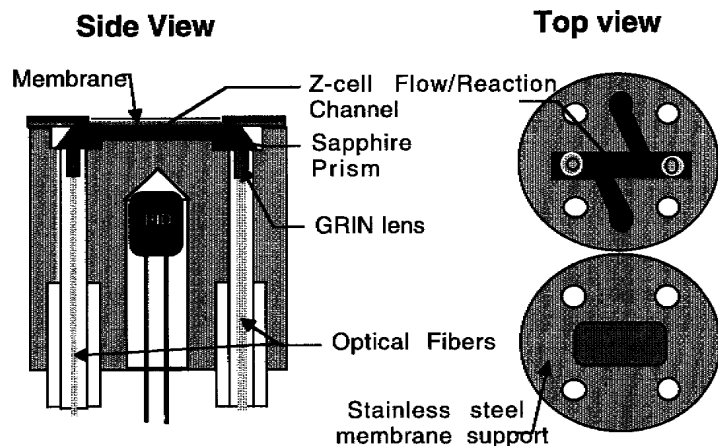
The basic concepts have been realized in both tubular liquid core waveguide and planar geometries, which share the common feature that the reaction and detection regions of the probe head are co-located. In a typical application the probe would be inserted into the sample matrix and fresh reagent would be pumped into the probe head. The analyte would then diffuse across the sampling membrane where it would react with the reagent to form a colored product. The differential optical absorption resulting from the product formation is measured spectroscopically. For each subsequent analysis, the reagent stream would be replenished, and the formed product flushed from the probe head, as the first step in the next analysis.

The ability to renew the reagent gives the sensor several important advantages over other types of sensors. The first advantage is that a wide range of reagent chemistries can potentially be employed for the detection of different analytes without the concerns about binding or immobilizing the reagent in the sensor head. The second advantage is that for each analysis the sensing mechanism is regenerated with fresh reagent so there are no problems associated with reversibility or baseline drift due to reagent use or loss. A third advantage is that the multiple analytes can be monitored sequentially by simply changing the reagent stream chemistries without any additional modification to the probe itself.

We have evaluated sensor geometries based upon a tubular semi-permeable material (a Teflon™ fluoropolymer resin) as the cladding of a liquid core waveguide. This geometry allows for a long optical pathlength resulting in high sensitivity, very large surface to volume ratio with relatively small diffusion distances, and is potentially a very rugged construction. A composite membrane has also been produced to enhance sensor response rate. The composite membrane is a multilayer membrane in which different layers have different functions. A thin layer of TEFLON™ AF-1600 with refractive index about 1.31 was coated inside the wall of porous polyethylene. In this form, the polyethylene provides mechanical support, while the AF is both the optical and semi-permeable interface. A composite membrane with a 14µm thick coating showed good waveguiding properties and very fast response rates.

More universally applicable, however, has been our efforts to realize a planar membrane probe. The component parts of a planar geometry sensor head are shown in Figure 1 below. The important features include 1) a Z-cell flow channel containing the reagent stream, 2) fiber optic based optical train to deliver and collect the spectroscopic signal, and 3) a membrane sampling system to isolate the reagent stream from the sample matrix

and to allow the analyte to move from the sample matrix into the reagent stream where it is detected. The fluid delivery and drain channels are not visible in the cross-sectional side view shown in Figure 1. The entire sensor head has a diameter of one-half inch and a length of about 2 inches. In most applications the sensor head is threaded onto a hollow stainless steel tube. This forms a convenient probe that can either be inserted directly into the sample or placed in a standard Swagelok™ fitting in a process stream. The membrane and support are attached to the end of the sensor head using four small screws.



**Figure 1.** Schematic view of the planar sensor head.

External to the sensor head are additional support systems which include 1) a fluid moving system to flush the Z-cell and provide fresh reagent for analysis, 2) a spectrometer for analyzing the spectral absorbance of the analyte/reagent reaction product, 3) a light source for the spectral analysis, 4) a computer system to control the operation of the instrument and collect and analyze the data, and 5) the necessary fluid, electrical, and optical fiber interconnects between the sensing head and the support systems.

A prototype of the planar probe was designed and built in collaboration with Sandia National Laboratory (SNL) and CPAC industrial sponsor companies, with funds from the DOE CMST-CP program. These prototypes have been field tested at several industrial and DOE sites.

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## THE VIABILITY OF INDUSTRIAL WATER REUSE

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Originally, water recycling was a term reserved to describe municipal wastewater that was purified to the point of being useful to water the lawns of golf courses and civic centers. Technological advancements over the past two decades have made it possible to recycle wastewater to be used even as drinking water! However, this is not yet being seriously adopted because of concerns over sufficient safeguards within the water treatment system to prevent adverse human health effects. Today, significant advancements are being made in the water treatment monitoring technologies that will provide these safeguards. Without robust and reliable process monitoring equipment, water reuse will remain feasible but not viable.

While direct potable water reuse is a goal for the future, there are currently many mechanisms that are used to recycle water. The most active are non essential water uses such as watering lawns, crop irrigation, and source water for industrial cooling towers. These uses of recycled water are of minor fiscal impact and are generally a part of water conservation efforts. The next use includes the support of current potable water systems for example, by injection of repurified water into the ground as a salt water intrusion barrier. This is used to protect coastal aquifers and has a moderate fiscal impact with a long term economic benefit. The final type of water reuse involves the repurification of wastewater to a quality that exceeds the quality of the original source water (potable water) for use in industrial processes. These types of water reuse often has immediate fiscal benefits and is the reason that industrial reuse programs are becoming so active today.

Clearly, industries are interested in optimizing processes, and even more so when the optimization results in growth and profitability. Companies that operate on a global scale understand the importance of obtaining quality raw materials worldwide. Industrial water reuse can provide solutions when water is a critical element of the manufacturing process. Today, industries that include petrochemical manufacturers, chemical producers, and the microelectronics industry have begun to reclaim and reuse water on large scale.

Reuse of wastewater as potable water has been active for some time but only on small scale. For example, the military has means to repurify water for ground troops and the space program is able to reuse water in space. It is critical to the troops, the astronauts, and the cosmonauts to have a reliable source of potable water.

A project conducted by the city of Denver proved conclusively that municipal wastewater could be recycled for human consumption. In San Diego, a pilot program is underway to demonstrate that they can reclaim wastewater to use as a source for replenishing above ground reservoirs. These projects found their outcomes dictated by their fiscal viability. For example, in Denver, there is no current potable water shortage. Further, the cost of developing new water sources is not that high. Therefore, the demand for recycling was not high enough to pay for the product. In San Diego, however, the cost of recycling the water is projected to be significantly less than finding additional sources of water to support a growing population. In the end, money, not environmental responsibility dictated the outcome of these programs.

The good news is that in several industries, water recycling is gaining acceptance as a prudent and cost effective way to control the quality of their water. Water can be used as a raw material or as part of the manufacturing process and is, therefore, important to control like any other raw material. Potable water quality is variable. This variability can lead to manufacturing problems or the need to develop expensive water purification systems. These systems, with minor modifications can be made to repurify potable water, or wastewater.

The microelectronics industry consumes large volumes of water. Since the elimination of chlorofluorocarbons (CFCs), high purity water is needed in nearly every part of the manufacturing process. A considerable amount of research has gone into this topic. For Japan, water reuse is mandatory. In the United States, several years ago, a number of negative experiences with first attempts at reclaiming process water sent the microelectronics industry into retreat. However, today water reuse in the microelectronics industry is quickly gaining acceptance.

One of the most critical elements to any recycle program is the ability to ensure water quality. This is universal and requires continuous, on-line monitoring capability of the product water. Although this sounds simple, it was not until recently that instruments had this kind of monitoring capability. Furthermore, there are a number of parameters that cannot be measured continuously on-line today and this can be a limitation for water reuse programs.

Total Organic Carbon (TOC) analyzers have been used for water testing from the late 1950s. Their primary use was in testing wastewater for carbon levels. These TOC analyzers were laboratory and not process control type equipment. In the 1970s a new technology was developed which allowed for non-quantitative TOC trend information to be monitored in very pure deionized water. This was a huge breakthrough that led to the acceptance of TOC as a viable monitoring technique.

However, in 1995, a new analyzer technology was presented that allowed quantitative TOC information to be taken on-line. And perhaps more importantly, this technology continuously monitors TOC in the process. This was a first. All of the other TOC technologies analyzed the water in batches making them prone to missing adverse events or excursions in the water system.

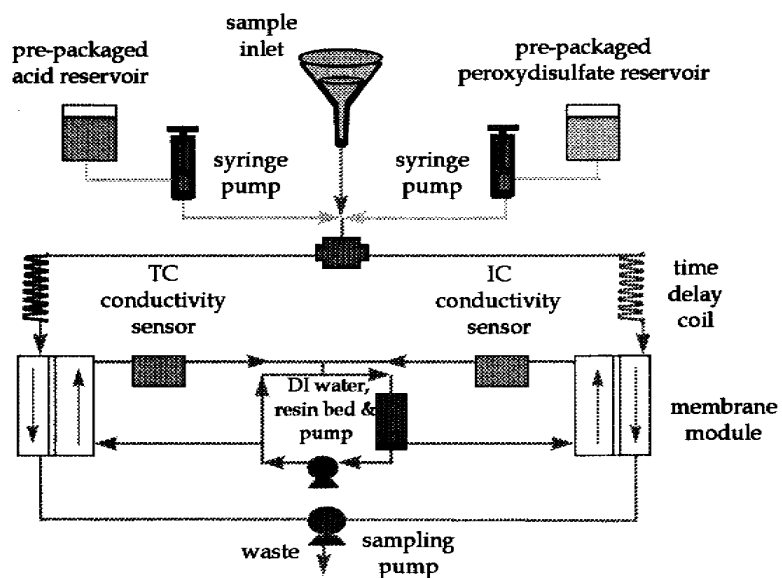
The principles of operation for this type of TOC analyzer have been described elsewhere. However, several changes have been made in the final product to adapt it to water reclaim. For example, in the microelectronics industry, the volume of water they reclaim can be as high as several thousand liters per minute. Therefore, the analysis time was reduced to 3.5 seconds to make it possible to make near instantaneous decisions about the quality of the water. A detailed schematic of the Sievers Turbo TOC analyzer is given in Figure 1.

Total Organic Carbon has become a critical parameter to monitor for water reclaim. The reasons differ for each industry. For example, potable water reuse will depend on TOC as evidence that their water treatment train has not failed. This is critical for preserving human health. The technique has proven extremely sensitive to water system problems and will ultimately provide confidence in the quality of the repurified water.

In the microelectronics industry, repurified water quality is also a concern, however, they are extremely sensitive to trace levels of organic material in the process water. These organics foul water purification equipment, and cause considerable reduction in product yields. For this industry, continuous TOC information is critical in routing the reclaimed water away from sensitive processes.

Reusing wastewater is coming of age. Technology exists that will allow the reuse of water for applications beyond watering the lawn. Reuse of wastewater has many advantages. It affords drought protection, provides consistent raw material (water) quality control, and allows water intensive industries to be more compatible with an environment limited in its supplies of high quality potable water.

Clearly the environment will benefit from water reuse programs. This is already taking place. However, the driving force for reusing water is generally fiscal combined with the positive environmental impact. The more that industries examine reuse as a positive impact on the bottom line, the more pleasing result for the environment.



**Figure 1.** Schematic of Sievers TOC Analyzer

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## COUPLING OF HEURISTIC DESIGN TECHNIQUES WITH RIGOROUS SIMULATOR-BASED OPTIMIZATION IN THE DESIGN OF GREEN CHEMICAL FACILITIES

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### Project Goals & Objectives

Despite rapid advances in computer software and hardware capabilities, the synthesis and optimization of "green" chemical processes is complicated by three interrelated issues. The first problem, which is not unique to green design but appears to be exacerbated by it, is the problem of *computational intractability*—that is, the existence of theoretical limits to computational solutions of large combinatorial problems<sup>1</sup>. The second issue is the problem of *data scarcity*: the toxicological, fate and transport, and physical property data required to model environmental significance of process design options adds to the already high cost of developing the models needed for rigorous optimization. The final issue is *data certainty*, since data uncertainties present in early stages of design can undermine the results of optimization efforts, increasing the perceived technical risk. Since this risk is, by definition, greater for innovative process designs, the result is a *de facto* barrier to the adoption of significant departures from the current design. Taken together, these issues present a significant challenge to the green design community.

Early work by Douglas<sup>2,3</sup> and others point out the potential value of heuristic ("rule-of-thumb") methods in addressing the problem of computational intractability in chemical process design. However, proper utilization of heuristic techniques can also be an effective means of dealing with the latter, more pragmatic problems. Our work seeks to explore the application of heuristic methods used in conjunction with more robust optimization methods as a means of dealing with the issue of data scarcity and data acquisition in green process design.

The goal of our work is develop a generalized set of design principles, or heuristics, which can be applied at early stages of chemical process design in order to facilitate the identification and subsequent evaluation of pollution prevention strategies. By applying these heuristics in early stages of design, sub-optimization problems can be defined which permit the evaluation of specific pollution prevention strategies via traditional optimization methods. Such heuristics also provide the designer with quick cognitive access to green design strategies, and can improve the overall quality of the design.

### Technical Approach

The process designer, especially in early stages of design, must contend with incomplete or inaccurate information about the process. If an environmental design review process is to be useful, it must be able to provide meaningful guidance even in situations where physical properties, kinetic data, and details of the process chemistry are unknown and/or uncertain.

In developing our design heuristics, we have attempted to adhere to some basic concepts:

Design heuristics should be based in practical experience of process plant operations, applying to *existing* technology and *current* design practice wherever possible. While emerging technologies can and often do play a role in pollution prevention, it is important to provide designers with practical solutions to common design problems.

While process plant experience is an important starting point, it is critical that the design principles also be rooted in *fundamental process phenomena* (e.g., kinetics, thermodynamics, and fluid dynamics). This permits the lessons of the process plant to be applied under an extended range of conditions, including in novel chemistries and processing environments where case study information rarely exists.

The value of heuristics can be enhanced by representing them as a *hierarchical structure*, starting with a core set of general guidelines which embody a larger number of more specific design strategies. As Pahl and Beitz<sup>4</sup> point out, there are important cognitive reasons for this: structuring the heuristics in this manner makes it easier for a designer to remember the concepts, and allows the designer to make incremental decisions about which strategy(ies) to apply rather than having to select strategies from the entire set.

The heuristic should reflect "hidden" wastes which may not appear on process flowsheets. Many wastes in process plants, especially those found in batch plants, occur during process transients, as a result of maintenance, or as fugitive emissions due to mechanical loss. It is important that these wastes be incorporated in the evaluation of design options.

Where possible, the design heuristics should suggest more rigorous simulation and optimization methods, so that the respective strengths of both heuristic and formal analytical methods are applied to the design problem.

Starting with these assumptions, we have reviewed approximately two hundred case studies and examples of pollution prevention in the process industries<sup>5,6,7</sup>. From these examples, we identified dozens of examples of process and equipment modifications which are applicable to process design. From these case studies, a series of candidate design principles, or heuristics, were developed. These were supplemented by design guidance provided in articles such as the excellent series by Nelson<sup>8</sup>, and more recent work by Mulholland, *et al*<sup>9</sup>.

### **Preliminary Finding**

Our work to date has resulted in the tentative identification of approximately three dozen specific design heuristics, around which we have identified the following high-level heuristics:

Design to reduce maintenance wastes. Maintenance-related wastes include solvents used for vessel cleaning, process fluids drained during servicing of pumps and heat exchangers, cleaning agents and abrasive materials, and materials such as tank heels, suspended solids, and sludge which accumulate in process vessels. Design strategies include providing interim storage for process and cleaning fluids, minimizing the volume of piping, using foul-resistant coatings and materials to reduce maintenance frequency, and insuring that frequently-cleaned vessels are provided with adequate drainage and line-of-sight clearance for high-pressure washing.

Design for selectivity. Another common source of wastes are byproducts created incidentally in separations equipment, heat exchangers, and other non-reactor vessels. Many of these operations result in the formation of byproducts from thermal decomposition or side reaction of process fluids. Design strategies include reduction of reboiler temperatures by elimination of process "hot spots," use of reduced distillation column pressures or specification of polymer-lined or high-polish finishes in heated vessels.

Design to reduce mechanical losses. Mechanical losses of materials include fugitive emissions from tank vents, pump seals, and valve packing; they can also include losses due to steam-injection vacuum pumps, sampling loop purges, and spillage from dry solids transfer operations. Design strategies include specification of vent recovery systems, specification of sealless pumps or closed-circuit seal rinses, and reducing valve and flange counts.

Design to reduce transient wastes. Transient wastes occur during process upsets and start-up/shut-down operations. Design strategies include providing interim storage and recycle loops for recovering off-spec product, implementing parallel reactor systems, and improving process control techniques.

It is expected that this list will be expanded significantly as we continue our analysis of case studies.

As suggested in the introduction to this paper, we have also begun to develop prescriptive approaches based on these heuristics which are designed to suggest rigorous sub-optimization problems which should be attempted in the evaluation of these strategies. For example, the kinetics of product degradation are often ignored in distillation column sizing, since the impact of this degradation on yield through the column itself is typically small. However, the presence of even a small amount of decomposition byproducts in an upstream column reboiler can significantly reduce the yield and increase the environmental impact of a process. According to several of the Design for Selectivity heuristics, however, thermal decomposition of product in reboilers should be considered an important design parameter. A "green design" approach to this important optimization problem might therefore include an explicit decomposition rate model along with the traditional VLE information.

### **Significance of Finding**

Designers have always made use of heuristic information in process design, often without being aware of it. Heuristic techniques permit conceptual and procedural simplification of the problem and serve as powerful

cognitive tools in design. The intent of this work is to simultaneously broaden the scope of environmental considerations which are included in process optimization while attempting to focus these optimization efforts on specific sub-problems which offer high potential for waste reduction and elimination. While much work remains to be done, our results thus far have demonstrated that anecdotal and case study information can be used to derive a relatively small number of broadly applicable green design heuristics.

The primary reason for incorporating pollution prevention into process development and design is one of cost effectiveness. Additional benefits may also be obtained when concurrent consideration of environmental issues with other engineering factors leads to quicker time-to-market, process innovation, improved quality of products, or increased efficiency.

Attention to these issues early in design requires the ability to make good decisions in the face of incomplete information, and to provide strong focus for subsequent detailed design, optimization, and data collection efforts. The coupling of heuristic methods with more robust optimization techniques provides an effective means for accomplishing this goal.

### Relevance to "Technology Vision 2020"

The discussion of chemical process modeling and simulation in "Technology Vision 2020" makes it clear that industry requires significant advances in order to be responsive to ever-shorter product cycles and increased cost and environmental concern over new product development. Many of these advances will occur due to increases in software and hardware technologies, but it is critical to recognize the intrinsic limitations to traditional optimization methods posed by computational intractability, data uncertainty, and the high cost of data acquisition. Integration of heuristic approaches with computational approaches to optimization holds promise of improving green design by reducing these limitations.

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## THE SYNGEN PROGRAM FOR GENERATING ALTERNATIVE SYNTHESSES

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A major goal of green chemistry is to find the most benign syntheses for any industrial chemical. Our objective in the SYNGEN project is to develop our computer program to meet this goal, to generate all the best synthesis routes to any target molecule of interest, and to assess their cost in both monetary and environmental terms. This account begins with the conceptual basis for generating these syntheses, and then briefly describes the present state of the SYNGEN program.

Since there are millions of possible syntheses for any target, this goal requires a logical protocol to survey all of them and locate only the few best ones. Exacting criteria are necessary to identify the best syntheses: these are taken to be the shortest ones, those with the fewest steps, and those using non-hazardous chemicals. The fewest steps not only implies the least work but also minimizes the amounts of solvents and reagents used and so minimizes their environmental impact.

To simplify this search at the outset such a protocol must stringently generalize the essential features of structures and reactions, to identify first only a few best general families of synthesis routes. These few will then only later be refined or expanded to full chemical detail.

In the SYNGEN program we envision the target structure as an assembly of merged starting material units, linked together by skeletal bonds (Figure 1). Conceptually we need to cut the target into real starting materials; then to assemble them back in syntheses which construct these skeletal links, mostly C-C bonds. Thus we need to keep an active catalog of available starting materials for constant comparison with new compounds as they are generated.

Synthesis is seen here as a skeletal concept. This skeletal focus arises since target molecules are bigger than their starting materials; hence the only obligatory reactions are those that construct the skeletal bonds linking the starting units together. The shortest syntheses then must be those which have no other reactions than these essential skeletal constructions. Hence an *ideal synthesis* is defined here as one in which every step makes a skeletal bond. Such ideal syntheses are rare but they constitute a demanding goal.

For the shortest syntheses, we seek the fewest starting materials so as to make the fewest skeletal bonds to join them. These will therefore be relatively large starting materials. Since the only obligatory reactions are skeletal bond constructions, SYNGEN seeks only routes which make at least one skeletal bond per step.

A survey of many published syntheses shows that in common practice a skeletal construction step is followed by functional group repair steps to prepare for the next construction. Indeed the average synthesis has two functional group repair steps for each construction step. The survey also shows that an average synthesis for non-aromatic targets constructs about one in three of the target's skeletal bonds, and uses starting materials with skeletons averaging only three carbons. *Hence the number of steps in an average synthesis is about equal to the number of skeletal bonds in the target.* This sets a standard for synthesis efficiency.

SYNGEN expects to find shorter syntheses for two reasons: its catalog of starting materials shows considerable functional variety up through five-carbon skeletons; and its criteria seek only ideal syntheses, constructing a skeletal bond in each step with no functional repair steps. If the millions of possible routes are systematically examined, there is reason to believe that a small number of such shortest routes will turn up, and this has been our experience to date.

This skeletal focus allows for the major simplification required to survey the enormous search space, namely by considering first only the skeletons: cutting the target skeleton into starting skeletons which are found in the catalog. For an efficient, convergent synthesis the target skeleton is cut into two intermediate pieces all possible ways, yielding a set of first cuts. Then for the second cuts, each intermediate piece is cut into two again, and the resultant sets of four starting skeletons are accepted only if all four are found in the catalog. For the shortest syntheses, no further cuts to smaller starting skeletons are made. At most six skeletal bonds will be cut and so no more than six construction steps will be required in the synthesis route.

This is diagrammed at the right in Figure 1 as an **Assembly Plan**. Each resultant set of four starting skeletons corresponds to a **bondset**, i.e., the sum of the target bonds cut. Many cuts will be rejected because all four starting skeletons are not in the catalog. Each bondset defines an assembly plan for linking available starting skeletons back into the target. Thus each ordered bondset/assembly plan defines a family of real syntheses which make those skeletal bonds designated by the bondset, applying actual chemistry to the skeletons, i.e., functional groups and reactions, in a variety of different combinations and steps.

The SYNGEN protocol has two phases, the first being these skeletal dissections into bondsets, then the second phase defining the functional groups on the skeletons of each bondset such that each step will construct a skeletal bond. An overview of the protocol is shown in Figure 2 for one particular, efficient bondset: three bonds in two cuts for the industrial synthesis of estrone.

For each bondset the second phase starts with the target functional groups and the first of the designated bonds: it derives for that bond all possible constructions and their substrate functional groups. Thus the program proceeds through the bondset bonds until it arrives at the functionality on the starting skeletons, i.e., real starting materials. Only if all four are available in the catalog is a route then accepted; again many will fail to find real, available starting materials and be discarded. With these stringent criteria (Figure 1) only the few shortest routes out of the millions possible will be generated.

For this second phase we need also to generalize the functional groups and how they change in reactions. In the SYNGEN system each skeletal carbon is abstracted to show only four kinds of bonds: R for s-bonds to other carbons (skeletal), P for p-bonds to other carbons (functional) and Z and H as functional bonds to other atoms, electronegative (X, O, S, N) or electropositive (H or metal), respectively. The numbers of each then add up to four, the valence of carbon.

This system creates a generalized definition of each of the carbons in a structure. This abstraction then becomes a brief digital description of the numbers of each kind of bond at each carbon in any structure, and allows a rapid computer manipulation of their changes in reactions. It also serves as a rigorous basis for fast comparison of the many generated structures with those in the catalog, which is indexed by the same digital abstraction.

Within this generalization all possible constructions of C-C bonds may be generated systematically from target or intermediate structures, and their chemical viability assessed, as indicated in Figure 2. The viability of the generated reactions may be validated by matching them against those in a large database of literature reactions indexed in the same system, to find their frequency of occurrence and average yield.

This logical basis allows SYNGEN to propose all the shortest alternative syntheses for any target from real starting materials, and to order them in terms of both cost and environmental impact.

The original SYNGEN program has been slowly developing from this basis over a number of years. At present the original SYNGEN program has been translated to a broader operating base and much expanded with new interfaces added for users to input a target structure and then display the generated bondsets, starting materials and routes. The program currently takes less than five minutes to generate all the routes for the input target.

The catalog of starting materials at present has about 6000 compounds registered with their prices. Data on their hazards is being assembled now as well to allow their assessment for environmental impact. Larger starting material databases exist and we shall incorporate these to enlarge our catalog.

The reaction database from our COGNOS reaction retrieval system is indexed in the same generalized digital format. It now has over 100,000 construction reactions and these are being embedded in SYNGEN for quick lookup to validate the generated reactions by reference to their literature precedents in the database.

In sum then the SYNGEN program intends to offer a new technical base for Technology Vision 2020, by providing a vision of all the possible alternative syntheses for any chemical, and so making available a choice of those that are the most environmentally benign.

## SYNTHESIS OF CHEMICAL PROCESSING SCHEMES: A PHILOSOPHY AND A TOOL FOR POLLUTION PREVENTION

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The type and amounts of wastes generated by a chemical process are the result of fundamental decisions made very early on during the stage of conceptualizing a process based on a set of chemical reactions, decision such as: selecting one among a set of alternative reaction pathways, using specific processing operations to isolate and purify a chemical product, employing specific solvents, catalysts, diluents, and other processing materials. In this paper, we will discuss how modern methodologies on selection of reaction pathways, process synthesis, materials selection, as well as tools for process modeling and simulation, such as the "BatchDesign-Kit", can be used to support the conceptualization of chemical processing schemes with Minimum Avoidable Pollution.

### From Reactions to Environmentally Benign Processes: Goals and Objectives in Process Development

As the production of chemicals undergoes a continuous specialization, to address the diversifying needs of the market-place, the economic opportunities for "being first in the market" are extremely attractive. In addition, the continuous evolution of product-recipes implies a much shorter life-cycle for a growing number of chemicals, than it has been traditionally the case, leading to a perpetual product/process evolution. In the presence of these economic dictates, the rational and systematic approach as well as the rapid execution of the chain of tasks, "*product development—process development—process design and engineering*" have become the pivotal elements of what chemical producers refer to as their *competitive edge* in the market place.

However, the manufacturing of specialty chemicals, traditionally carried out through batch processing schemes, produces *very large amounts of wastes per unit product*. In addition, many of the materials they employ for processing efficiencies tend to have fairly adverse ecological impact (e.g. toxicity, flammability, low biodegradability, emissions to the atmosphere of volatile compounds). As ecological regulations become more stringent, chemicals producers need to depart from existing practices, and concentrate on changing the way they develop products and processes, if they are to capture the attractive market opportunities. End-of-pipe treatment of wastes, or/and relocation of manufacturing facilities to places with more permissive environmental regulations, are temporary and in some respect counter-productive solutions.

The Pollution Prevention Act, passed by the Congress in 1990, is but a small leap of intellect from the previous well established principle of *waste minimization*. It is easy to set the so-called *Maximum Achievable Control Technology* (MACT) standards, but nobody has put forward specific guidelines on how to set *Minimum Achievable Pollution Prevention Technology* (MAPPT) standards. Nevertheless, industrial experience during the last 4-5 years has indicated that creative revamps of processing schemes have led to reductions in the waste loads with accompanying improvements in processing efficiencies. Harvesting these "low hanging fruits" has not been very difficult. The question of how does one push further the envelop of pollution prevention remains open.

The central conjecture of our work has been the assertion that, *productivity improvements and opportunities for shortening the time-to-market can make a strong case for pollution prevention*. Such conjecture goes contrary to the established wisdom. However, the use of benign materials could lead to higher processing efficiencies, Two are the main consequences of the above conjecture:

- Self-imposed design constraints, reflecting the desired levels of pollution prevention, can fuel major revamping of the conceptual processing scheme one employs for the production of a specialty chemical
- Systematic approaches are needed for the conceptual synthesis and evaluation of alternative benign batch processing schemes.

These two consequences have provided the motivational core of the technical work carried out at MIT over the last 4 years.

### Systematic Synthesis of Processing Schemes: The Core of the Technical Approach

The efficiency of a batch processing scheme for the manufacturing of specialty chemicals and the amounts of the generated wastes are directly related to the type of operations employed, and the type and amount of the various materials used (or, produced) in the process, such as; raw materials, homogeneous catalysts, solvents, inerts, diluents, storage media, washing and cleaning agents, heat carriers, and utilities (e.g. purging/venting agents, refrigerants, coolants such as brine). Consequently, the development of environmentally benign processes with high processing efficiencies requires a systematic approach for the simultaneous, (a) synthesis of conceptual processing schemes, i.e. the selection of the "best" operations and their sequencing, and (b) selection/design of the "best" materials.

Raw Materials and the Reaction Network. Starting with the desired final product one can employ the well established *retrosynthetic* approaches to identify the potential *precursor-intermediate* products, until one reaches a given set of easily available initial reagents. The synthetic algorithms of Mavrovouniotis (Mavrovouniotis and Bonvin, 1995) can also be used to ascertain the completeness and consistency of the generated reaction pathways.

The feasibility and attractiveness of each alternative sequence of chemical reactions depends on the following considerations: (a) overall equilibrium conversion yields from the raw materials to the desired product, (b) relative reaction rates to the desired product (intermediate or final) and the various by-products, i.e. the relative reaction sensitivities, (c) the prices of the various raw materials, (d) the ecological characteristics of all chemicals; raw materials, intermediates, and by-products. Although the selection of the best does involve a large combinatorial problem, the pivotal impediment has been the estimation of the relative reaction rates in various solvents, and the estimation of the ecological properties. Both of these difficulties have been addressed by our research work with satisfactory success.

Plant-Wide Selection of Solvents. Solvents are used in a batch processing scheme to: (a) store raw materials, (b) to enhance reaction rates and selectivities, (c) to quench a reaction, (d) stabilize the formation of the desired product, (e) extract the desired product or by-products from the reacting mixture, (f) provide the medium for the crystallization of a product, (g) prepare filters for the filtering operation, (h) wash the crystals from a filter, (i) clean process vessels from impurities, (j) break azeotropes, and (k) act as transfer media for potentially hazardous compounds.

Traditionally, the selection of solvents has been addressed within the scope of specific process operations. As a result, a solvent which is excellent for the enhancement of reaction rates and selectivities could create insurmountable problems for the downstream processing operations. Consequently, only a plant-wide scope for the selection of the best solvents could lead to consistent and optimal results. All solvents should have properties, which satisfy three groups of desired specifications; processing, environmental, safety, and health related. The processing requirements are dictated by the roles that particular solvents serve. The selection of the solvents which satisfy all the desired physical and ecological constraints is a fairly complex combinatorial problem, and is hampered by missing data, or methodologies for the estimation of certain physical properties. An integrated usage of (a) effective physical properties estimation models (including some with molecular and atom-bonds specialized representations) and (b) large databases of physical properties have provided an effective framework for the estimation of the requisite physical properties.

Furthermore, in order to overcome the combinatorial complexity of the solvent selection problem we have pursued a hierarchical approach, which proceeds in the following three levels (Modi et al., 1995):

Level-1: Given the description of a batch process, identify all the solvent-based processing tasks.

Level-2: Screen-out solvents which violate task-level constraints; processing or ecological.

Level-3: Screen-out solvents which violate plant-wide constraints.

Synthesis of Processing Schemes. The systematic synthesis of batch processing schemes proceeds in a two step approach: (a) Synthesize the processing schemes with Zero Avoidable Pollution (ZAP), i.e. schemes with full recovery and recycle of all processing materials besides the reaction by-products. (b) Evolve from the ZAP processing scheme to the Minimum Avoidable Pollution design, one that establishes the optimal trade-off between economics and type/amounts of generated wastes.

The synthesis of ZAP processes goes through a hierarchical sequence of design decisions at the following levels:

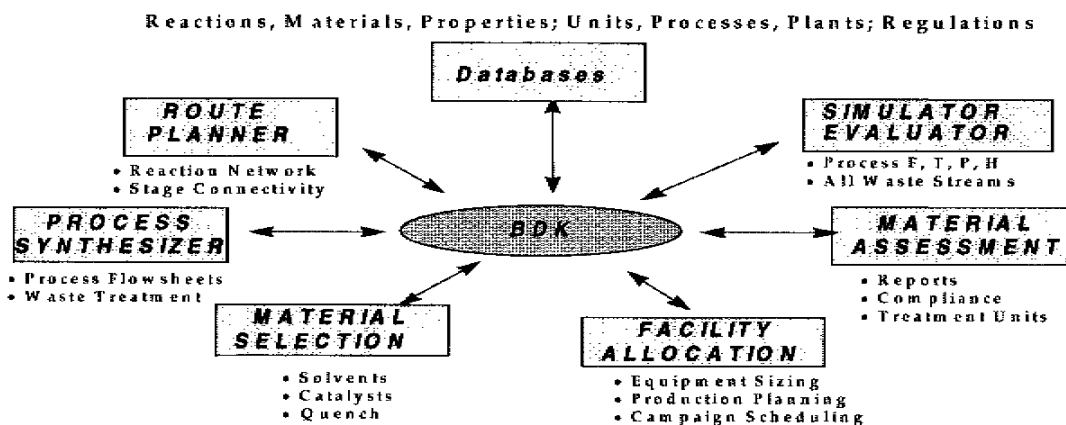
(1) Generation of the multi-stage plant, which results from the selected sequence of reaction steps. (2) Hierarchical decomposition and synthesis of conceptual designs for each stage of the plant. (3) Integration of the process stage flowsheets. (4) Generation and evaluation of improved alternatives. The first prototype of this design philosophy for batch processes can be found in Linninger et al. (1995).

The evolution of ZAP processes to schemes with Minimum Avoidable Pollution and thus better trade-offs between economics and ecological considerations, is guided by the lexicographic goal programming (Linninger et al. (1995)), allowing the designer to relax the design objectives in a sequence of increasing importance.

**The "Atom-Bonds Conjugations" Approach.** The discussion above has revealed the need for the estimation of the values of several physical properties, both for pure components and mixtures, the estimation of reaction rates in solvents, and the assessment of several ecological characteristics. Following the formalism of the Atom-Bonds Conjugation (ABC) approach (Mavrovouniotis, 1990), the properties of a molecule (dominant structure) are computed by computing the properties of its conjugate structures, i.e. the delocalizations of  $\pi$ -electrons or  $\sigma$ -electrons in chemical bonds. The ABC approach has been shown to yield higher accuracy in the estimation of physical properties than group contribution methods. It also allows distinction between isomers and the computation of properties of unstable and charged species, since it employs conjugate structures that are inherently charged with bonds, partially formed or destroyed, instead of groups. Subsequent work extended ABC to ionic species, mixtures and recently the estimation of rates for reactions in gas phases or solvents.

**The "BatchDesign-Kit" (BDK).** This is an integrated set of software components, which provide the computer-aided implementation of the methodologies sketched in the previous paragraphs. Figure 1 provides an overview of the system's components and their interrelationships. Presently, a limited version of BDK is being tested by chemists and engineers involved with batch process development of pharmaceuticals, agricultural, and specialty chemicals in more than 20 companies.

Unlike its counterparts in continuous process simulation and design, BDK has pioneered some new metaphors for the description of batch processes, e.g. the *Process Sequence Diagram*, a two-dimensional depiction of the material flows in time and among processing facilities, the *BatchSheet* a textual description of the recipe with the various operations in a batch process, the *Materials Model* which constitutes the basis for the state-task network of materials transformations occurring in a batch process, etc. With 53 operations in its repertory, extensive databases for materials properties, reactions, utilities, experimental data for liquid-liquid and vapor-liquid equilibria, BDK offers a variety of facilities for the synthesis, simulation, economic and ecological assessment of batch processing schemes.



**Figure 1.** The overall structure and components of "BatchDesign-Kit"

### Relevance to the "Technology Vision 2020"

In this paper we have tried to outline a broad, in scope, effort that we have undertaken over the last 4 years, in order to systematize the activities involved in various phases of the so called Batch Process Development. Both in terms of methodologies as well as in terms of the resulting enabling technologies, the aims and objectives of our work are very closely in line with those of the "Technology Vision 2020" as is described in the Section "Process Science and Engineering Technology" of the Chapter on "Enabling Technologies", where "...the



development of appropriate design principles, tools, systems... (leading to) Reduction of the commercialization process for new products and processes..." are identified as essential for the maintenance of industrial competitiveness. The incorporation of multiple objectives, e.g. economics, ecological, operational, lends an additional dimension to the generic statement of aims and offers challenges and opportunities that can only be addressed through an integrative philosophy of disciplines, as the overview of our activities in the previous sections has indicated.

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